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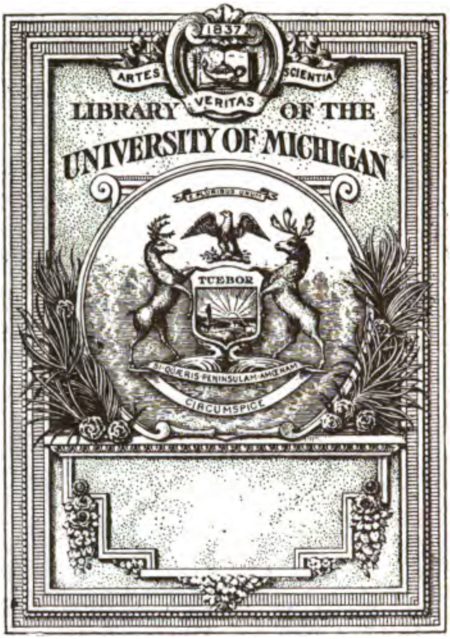

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INDUSTRIAL CHEMISTRY

BEING A SERIES OF VOLUMES GIVING A
COMPREHENSIVE SURVEY OF

THE CHEMICAL INDUSTRIES

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INDUSTRIAL ELECTROMETALLURGY

INCLUDING

ELECTROLYTIC AND ELECTROTHERMAL PROCESSES

BY

ERIC K. RIDEAL, M.A. (CANTAB.), PH.D., F.I.C.

JOINT AUTHOR WITH S. RIDEAL OF "WATER SUPPLIES"

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GENERAL PREFACE

THE rapid development of Applied Chemistry in recent years has brought about a revolution in all branches of technology. This growth has been accelerated during the war, and the British Empire has now an opportunity of increasing its industrial output by the application of this knowledge to the raw materials available in the different parts of the world. The subject in this series of handbooks will be treated from the chemical rather than the engineering standpoint. The industrial aspect will also be more prominent than that of the laboratory. Each volume will be complete in itself, and will give a general survey of the industry, showing how chemical principles have been applied and have affected manufacture. The influence of new inventions on the development of the industry will be shown, as also the effect of industrial requirements in stimulating invention. Historical notes will be a feature in dealing with the different branches of the subject, but they will be kept within moderate limits. Present tendencies and possible future developments will have attention, and some space will be devoted to a comparison of industrial methods and progress in the chief producing countries. There will be a general bibliography, and also a select bibliography to follow each section. Statistical information will only be introduced in so far as it serves to illustrate the line of argument.

Each book will be divided into sections instead of chapters, and the sections will deal with separate branches of the subject in the manner of a special article or monograph. An attempt will, in fact, be made to get away from the orthodox textbook manner, not only to make the treatment original, but also to appeal to the very large class of readers already possessing good textbooks, of which there are quite sufficient. The books should also be found useful by men of affairs having no special technical knowledge, but who may require from time to time to refer to technical matters in a book of moderate compass, with references to the large standard works for fuller details on special points if required.

To the advanced student the books should be especially valuable. His mind is often crammed with the hard facts and details of his subject which crowd out the power of realizing the industry as a whole. These books are intended to remedy such a state of affairs. While recapitulating the essential basic facts, they will aim at presenting the reality of the living industry. It has long been a drawback of our technical education that the college graduate, on commencing his industrial career, is positively handicapped by his academic knowledge because of his lack of information on current industrial conditions. A book giving a comprehensive survey of the industry can be of very material assistance to the student as an adjunct to his ordinary textbooks, and this is one of the chief objects of the present series. Those actually engaged in the industry who have specialized in rather narrow limits will probably find these books more readable than the larger textbooks when they wish to refresh their memories in regard to branches of the subject with which they are not immediately concerned.

The volume will also serve as a guide to the standard literature of the subject, and prove of value to the consultant, so that, having obtained a comprehensive view of the whole industry, he can go at once to the proper authorities for more elaborate information on special points, and thus save a couple of days spent in hunting through the libraries of scientific societies.

As far as this country is concerned, it is believed that the general scheme of this series of handbooks is unique, and it is confidently hoped that it will supply mental munitions for the coming industrial war. I have been fortunate in securing writers for the different volumes who are specially connected with the several departments of Industrial Chemistry, and trust that the whole series will contribute to the further development of applied chemistry throughout the Empire.

SAMUEL RIDEAL.

AUTHOR'S PREFACE

AMONGST the many branches of applied chemistry electrometallurgy has shown a great technical development, and in the following pages an endeavour has been made to indicate both the limits and possibilities of the application of electrolytic and electrothermal methods in this domain.

It is a matter of past regret and present concern that Electrochemistry has not yet, except in one or two exceptional cases, been raised to the dignified standing of a "subject" in our English higher educational system. As a result electrochemical considerations receive but scant attention, usually being confined to a few lectures in a course covering the whole of physical chemistry.

Notwithstanding the fact that there exists an excellent bibliography of text-books on theoretical electrochemistry, this lack of a personal element in the teaching has been sufficient to eliminate the English research student from the field.

As a result the English Industry has suffered in having either to purchase foreign processes or to waste both time and money in experimental work carried out by investigators ill equipped with the requisite knowledge. It must not be forgotten that in the English-speaking countries there are sources of power and raw materials in very great variety, awaiting development at the hands of those who are capable of taking part in the great post-war period of reconstruction.

In many specific cases electrochemical processes offer both economic, æsthetic, and industrial advantages over older chemical or metallurgical treatment, and in the development of old processes or in the exploitation of new ones, it is the hope of the author that the case for electrochemistry may have both due and deliberated consideration, and that the present volume may contribute to this end.

In the sections on Electrolytic processes, the normal hydrogen electrode has been taken as the arbitrary standard of zero potential difference, whilst the conventional positive sign is placed before the electrolytic potentials of those metals which possess an electrolytic solution pressure greater than that of hydrogen, *i.e.* those elements which are most chemically active, whilst the more noble elements are given a negative value on account of their small solution pressures.

In many of the calculations the heats of formation of certain compounds form the basis for the derivation of their decomposition potentials. This method, as shown in the introduction, although not strictly correct, usually gives results sufficiently accurate for practical purposes where direct experimental observation must necessarily include small irreversible electrode effects. Special emphasis has been laid upon the influence of colloids in electrolytic deposition, whilst in electrothermal processes the dissociation of many stable compounds at high temperatures, and the application of the partition coefficient of substances between immiscible slags and metals, have been used to assist in the elucidation of the reactions involved.

E. K. R.

LONDON,
June, 1918.

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INDUSTRIAL ELECTROMETALLURGY

INTRODUCTION

The foundations of the general principles of electro-metallurgy were laid by Michael Faraday in 1833, who introduced the present nomenclature, *e.g.* such terms as electrolyte electrode, cathode, anion, and gave us the fundamental quantitative laws on which both the science and industry of electrolytic processes are founded. It is frequently forgotten that it is to Faraday we owe the important generalization that a definite and unalterable quantity of electricity is associated with each valency of an element, the first tangible suggestion of the atomistic or electronic theory of electricity.

In 1853 Hittorf noticed that the concentration of the solute in the solvent altered during electrolysis. The concentration of copper sulphate, for example, in aqueous solution increases at the anode and decreases at the cathode when such a solution is subjected to electrolysis.

By a series of experiments he was able to calculate the transport number of the ions, whilst Kohlrausch a few years later (1869), by an elaborate investigation on the molecular conductivities of dilute solutions, was able to determine the values of the velocities of the ions under a definite potential gradient. From Hittorf's and Kohlrausch's figures it is possible to calculate the actual ionic velocities in cms. per hour under a potential gradient of one volt per cm. in dilute solutions. The following figures were obtained for solutions at 18° C.

Cations.	Anions.
$\dot{\mathrm{H}}$ 10·8	OH' 5·6
$\dot{\mathrm{K}}$ 2·05	Cl' 2·12
$\dot{\mathrm{Na}}$ 1·16	NO'_3 1·91
$\dot{\mathrm{Ag}}$ 1·66	

The calculated figures were confirmed by actual measurement of the migration velocity of the ions in solution by Lodge, Whetham, Steele, and others.

Up to this stage in the development in the principles of electro-chemistry no hypothesis as to the state of the solute in the solvent was necessary. In 1887 the Grotthusian hypothesis of electrolytic conduction was replaced by the dissociation theory of Arrhenius and Van 't Hoff. According to this theory a salt when dissolved in an ionizing solvent is partially dissociated into free ions, according to the following scheme—

$$MX \rightleftarrows \dot{M} + X'$$

Equilibrium is established in accordance with the laws of mass action, and the solution as a whole is electrically neutral.

A further advance was made in the subject by Van 't Hoff, who applied the gas laws to substances in solution. The concentration of the reacting constituents, undissociated molecules or ions in the solvent were regarded as equivalent to the concentrations or partial pressures of gases in a gaseous mixture.

There is no doubt that this conception has been of great service to the electro-chemist, and the results obtained by a rigorous application of the gas laws to dilute solutions have been not only extremely varied, but of far-reaching importance.

It is somewhat unfortunate that the development of the ionic theory originally suggested by Arrhenius and Van 't Hoff was chiefly accomplished in Germany, where frequently a somewhat pedantic train of thought tends to exclude other important factors from due consideration. In this case the function of the solvent was entirely neglected and treated rather as the convenient vacuum in which gases could be distributed. Many discrepancies were noticed between the experimental and calculated results, especially when dealing with strong electrolytes, and as a result ingenious theories and formulæ were proposed to square the facts either frankly empirical or based on some pseudoscientific generalization from Van der Waal's equation.

The experimental work of Walden (1904, *et seq.*) on the conductivities of electrolytes in various solvents indicated that the theory could not be retained in the simple form as originally stated by Arrhenius and Van 't Hoff. At the present time no new theory has been proposed capable of the simple thermodynamic treatment which was one of the great advantages of the old one, but at any rate we must now consider the problem in a new light, as one in which the solvent itself performs important, if not the most important, functions.

Ionization must be regarded as taking place subsequent to solution (usually hydration) of the solute according to the following scheme—

$$MX \rightarrow MX(H_2O)_m \rightleftarrows \dot{M}(H_2O)_x + X'(H_2O)$$

both the undissociated salt and the ions being surrounded by envelopes of the solvent. The nature of the forces holding the envelope round the solute, as well as the number of solvent molecules in each envelope, is as yet a matter of uncertainty, but it seems probable, from a consideration of the ionic mobilities, that the ionic hydration numbers are small, rising to 6 or 9 molecules per ion in the case of the ions of small atomic weight, *e.g.* Li· or F′, and may be entirely absent in the heavier ones, such as Cs· and I′.

ELECTROLYTIC POTENTIALS.

In addition to the ionic theory, the hypothesis of electrode "solution pressure" advanced by Nernst in 1889 has been of great assistance in developing the science. On this hypothesis, all metals possess a solution pressure or a tendency to drive ions into solution. Since the metallic ions leaving the metal are positively charged, the electrons or negative charges are kept in the metal; metallic ions are consequently forced into solution until the potential difference between the metal and layer of solution in contact with the metal is great enough to prevent the further discharge of metallic ions.

Imagine the transfer of δn gm. ions of a v valent metal to pass from the electrode to the solution. The electrical work is $evV\delta n$ where $ve\delta n$ is the charge carried by δn gm. ions. This transfer is also equivalent to bringing δn gm. ions from the solution pressure P to the solution of osmotic pressure αC, where C is the concentration of the salt in the solvent and α its degree of ionization, and equal to

$$\delta n \mathrm{RT} \log \frac{\mathrm{P}}{\alpha \mathrm{C}}$$

By the principle of virtual work,

$$\mathrm{V}ev\delta n = \delta n \mathrm{RT} \log \frac{\mathrm{P}}{\alpha \mathrm{C}} \quad \text{or} \quad \mathrm{V} = \frac{\mathrm{RT}}{ve} \log \frac{\mathrm{P}}{\alpha \mathrm{C}}$$

We can also arrive at a similar relationship in the following manner :—

If a metal of valency v be placed in an electrolyte containing its ions, and equilibrium is established when the difference of potential between the metal and solution has risen to a value V and the ionic concentration of the metal in the solution has risen to αC, and further, if $\overset{+}{\mu}$ and μ be the chemical potentials of the ions in the solution and the uncharged molecules in the metal respectively, with an electric charge ve on each ion, equilibrium is established when

$$\overset{+}{\mu} - \mu = \mathrm{V}ve$$

But

$$\overset{+}{\mu} = \overset{+}{\mu}_0 + \mathrm{RT} \log \alpha \mathrm{C}$$

hence

$$\mathrm{V} = -\frac{(\overset{+}{\mu}_0 - \mu) + \mathrm{RT} \log \alpha \mathrm{C}}{ve}$$

putting

$$\mu - \overset{+}{\mu}_0 = \mathrm{RT} \log \mathrm{K}$$

$$\mathrm{V} = \frac{\mathrm{RT}}{ve} \log \frac{\mathrm{K}}{\alpha \mathrm{C}}$$

where K is to be regarded as the solubility constant of the metal in the form of metallic ions.

The electrolytic solution pressures of the metals as calculated from the measurements of the electrode potentials vary very considerably; for example, P for zinc is equal to 10^{17} atmospheres and for palladium equal to 10^{-31} atmospheres.

It is evident that although the conception of electrolytic solution pressure is a convenient one, it cannot be a true representation of the facts, and it would appear more reasonable to adopt Smit's and Van Laar's suggestion of replacing the term solution pressure P by K, the solubility constant of the metal in the form of its metallic ions. In those cases where the electrode is composed of an alloy or amalgam of two or more metals, the theoretical calculation of the electrolytic potentials has been made by Van Laar,* to whom the reader is referred.

In the following pages the electrolytic potentials of the metals in a solution of normal ion concentration are all referred to the normal hydrogen electrode, which is taken at the arbitrary value

$$E_h = \frac{RT}{e} \log \frac{\text{P hydrogen at 1 atmosphere}}{\text{C normal hydrogen ion solution}} = 0.$$

The determination of the true value of electrolytic potentials is a matter of some difficulty, since a zero E.M.F. between a metal and solutions of its salts cannot readily be obtained; but the dropping electrode of Paschen and Palmaer † may be considered as being the most satisfactory attempt to devise an auxiliary electrode comprising electrode and electrolyte of zero potential difference.

The calculation of the potential difference between two electrodes in the same or different electrolytes separated by a diaphragm, by means of the equations developed by Nernst, Henderson and Planck, can be obtained not only from a knowledge of the respective electrolytic solution pressures of the metals, the concentrations of the solutions and the mobility of the respective ions, but also as shown by Helmholtz and Thomson in 1847, from a knowledge of the heat of reaction.

If we consider the simple system, copper/copper sulphate/

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* *Elektrochemie*, Amsterdam, 1907. † *Zeit. Phys. Chem.*, **25**, 265, 1895.

zinc sulphate/zinc, the zinc and copper being joined by a wire, and imagine it at work at t* until δn gms. of zinc are dissolved and copper deposited, we then raise the temperature to $t+\delta t$ and pass a current through the cell so as to redeposit the δn gm. ions of zinc and dissolve the same amount of copper, subsequently allowing the cell to cool again to t.

If the E.M.F. of the cell at t is π volts, at $t+\delta t$, $\pi-\delta\pi$, the electrical work done by the cell is equal to $ve\delta n\pi$, where v is the valency of the metal, in this case 2, and e is the charge per gm. equivalent of a monovalent element; whilst the chemical work is equal to δnq, where q is the heat of solution of a gm. atom of zinc—the heat of solution of a gm. atom of copper.

The energy given out by the cell is consequently $\delta n(q-e\pi v)$. The heat absorbed at the higher temperature will be in a similar manner equal to $\delta n(q-ve(\pi+\delta\pi))$ if the heat of reaction does not change sensibly with the temperature.

During the cycle, the external work performed is equal to $v\delta ne\delta\pi$ and the quantity of heat given out at the lower temperature is $\delta n(q-e\pi v)$.

Now
$$\frac{v\delta ne\delta\pi}{\delta t}=\frac{\delta n(q-e\pi v)}{t}$$

or
$$\pi=\frac{q}{ve}+t\frac{\delta\pi}{\delta t}$$

In many cases the temperature coefficient $\frac{\delta\pi}{\delta t}$ is so small that the term $t\frac{\delta\pi}{\delta t}$ may be neglected for approximate calculations of π.

OVERPOTENTIAL AND PASSIVITY.

With a potential difference smaller than that calculated, the passage of the current is only associated with concentration changes in the electrolyte, provided of course that

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* t is measured in degrees on the absolute temperature scale.

other ions capable of being discharged at the lower potential are not present in the electrolyte. For example, in the electrolysis of dilute sulphuric acid between platinum electrodes, the following ionic discharges take place with increasing applied potential difference.

P.D. in volts.	Ionic discharge.
1·08	$\dot{H}\rightarrow H_2$ $O''\rightarrow O_2$
1·67	$2OH'\rightarrow H_2O+O_2$ $\dot{H}\rightarrow H_2$
1·95	$SO_4''\rightarrow H_2SO_4+O_2$ $\dot{H}\rightarrow H_2$
2·60	$HSO_4'\rightarrow HSO_4$ and $H_2S_2O_8$ $\dot{H}\rightarrow H_2$
2·83	$\dot{H}\rightarrow H_2$ $3O''\rightarrow O_3$

In practice a potential difference considerably higher than that calculated has to be applied to bring about electro-deposition at an economic rate. The uses of depolarizing agents added to the electrolytes in order to reduce the applied voltages necessary for electrolysis, and thus lower the electrical energy consumption at the expense of the depolarizer, will be dealt with in subsequent sections.

Frequently the excess potential difference found necessary can be traced to the occurrence of irreversible phenomena taking place at the surface of the electrodes. Apart from the general one of the Joule heat loss due to the resistance of the circuit, those causes of discrepancy between theory and practice may be accounted for by one of the following factors :—

Overpotential.—In those processes where cathode hydrogen is liberated, it has been noted that the P.D. necessary for hydrogen liberation, when the same electrolyte is used and identical anodic reactions take place, is not independent of the nature of the cathode. The theoretical applied E.M.F. has always to be increased by a certain definite amount for each particular metal. According to

Caspari, the following are the values of the overpotential η :—

Metal.	η in volts.
Hg	1·3
Pb	1·3
Cd	1·22
Sn	1·15
Ni	1·00
Zn	0·80
Cu	0·19
Pt (bright)	0·07
Pt (black)	0·00

No satisfactory explanation for this phenomenon is as yet forthcoming, although attempts have been made to correlate the η values with the heat of formation of hypothetical hydrides, with surface tensions, with the formation of absorbed gas and with the diffusivities of gas molecules and the gas ions in the metal. Advantage is taken of the high overpotentials exhibited by certain metals in certain electrolytic reduction processes and in the technical deposition of zinc and cadmium.

Passivity.—As in the case of cathodic hydrogen, the anodic evolution of oxygen is also associated with irreversible overpotential phenomena, usually, however, of quite inconsiderable magnitude A more serious disturbance of anodic processes is the occurrence of passivity. In certain electrolytes metals may exhibit no tendency to anodic solution ; the metal appears more " noble " than is actually the case. Electrolytes containing oxidizing acids are more prone to cause this phenomenon than others, and although probably all metals may be passified by suitable treatment, the following exhibit the characteristics to a marked degree : iron, aluminium, cobalt, chromium, platinum, tungsten, and molybdenum. Various theories have been proposed to account for the phenomenon of passivity, which have been summarized in the "Transactions of the Faraday Society" for 1916 ; amongst the more important may be mentioned :

1. The formation of a gas film on the surface.

2. The formation of an oxide film.

3. The conversion of the surface metal into an allotropic modification, of which the electrolytic solution pressure is low.

4. The velocity of ionization or hydration of the ion is retarded below its normal speed.

Reaction Velocity.—The maximum speed at which any change involving a cycle of operations may be made to take place is set by the maximum velocity of the slowest intermediary link. This generalization is frequently overlooked in electro-chemical process, but is nevertheless one of the most important factors in the cause of electrical inefficiency, as may be indicated by the following examples :

If we use an alternating current to perform the electrolysis of copper sulphate with copper electrodes, we can imagine that when one electrode becomes the anode the SO_4'' ion will be discharged, forming cupric sulphate with solution of the metal; at the next instant the current is reversed, and the cupric ion will be discharged The sum total of the two reactions can be represented as follows :

$$Cu \rightleftarrows Cu^{\cdot\cdot}$$

It is evident that no change in weight of the electrode should take place if the ions simply oscillate to and fro from the electrode to the solution, but if they are removed whilst in the solution by hydration, unless hydration occurs instantaneously, a net loss in weight will result. Leblanc found by experiment that the alternations of a current of a periodicity of 50 and above were sufficiently quick to prevent such a loss, whilst the ions were in solution, but for less frequent alternations solution did actually take place. If potassium cyanide were present in the electrolyte, solution occurred up to 500 periods, but ceased at 10,000. From these figures it is clear that the rates of transformation of the various modifications into each other, which metallic copper has to undergo before it passes from the anode to the cathode in an electrolytic cell, are by no means instantaneous, and do actually set a limit to the velocity of electrolysis.

ELECTROLYSIS IN FUSED ELECTROLYTES AND ELECTROTHERMICS.

The isolation of the alkali metals by electrolysis of the fused hydroxides, and the technical method of manufacture adopted at the present day, was first accomplished by Sir H. Davy (1800 to 1810). A systematic investigation of the properties of the fused salts has been made by Lorenz and his pupils, who showed the general applicability of Faraday's laws to these electrolytes. In general the conductivity of fused solutions is much superior to aqueous solutions, but at the same time, owing to various disturbing influences, the current efficiency is usually lower. The following are the more important causes of low efficiencies :—

1. *Evaporation of the deposited metal.*—A very considerable loss may occur due to vaporization of the deposited metal. This factor becomes increasingly important the higher the melting point of the metal, since the temperature interval through which the liquid exerts an appreciable vapour pressure is always larger for metals of low melting point.

2. *Chemical side reactions.*—In fused electrolytes the intermediary formation of sub-salts unstable in aqueous solutions is of somewhat frequent occurrence. A notable example is found during the electrolysis of calcium chloride, where the cathode formation of the coloured subchloride, CaCl, causes a reduction in the yield of metal.

3. *Cloud formation.*—During electrolysis of certain metals, especially lead, in fused electrolytes containing alkalis, the precipitated metal will frequently not coalesce, but is dissipated through the electrolyte in the form of a fine cloud or mist. It is as yet uncertain whether the cloud consists entirely of the metal cathodically deposited in the form of a colloidal solution or whether it contains a small quantity of the alkali metal, alloyed or combined with it. To obviate or minimize cloud formation, the temperature of the electrolyte should be maintained as low as possible.

4. *Solution of the Metal in the Electrolyte.*—As in

the case of aqueous electrolytes, the determination of the electrolytic potentials of the metals in fused solutions has been attempted, but no high degree of accuracy was obtained owing to experimental difficulties in connection with the construction of a suitable auxiliary cathode, and the rapidity of diffusion of the fused electrolytes. The values of the electrolytic potentials are usually approximated by interpolation from the figures obtained from amalgams of known composition in aqueous electrolytes.

The development of electro-thermal processes has, as is indicated by its name, been confined to the chemical effects produced by the Joule heat liberated by the passage of the current through resistances either of the first or second class. The upper temperature limit obtainable in an electric furnace is that temperature at which the rate of sublimation of carbon becomes appreciable and has been estimated at from 3000° C. to 3600° C. By this means the preparation of a number of high-temperature products hitherto unprocurable has been a matter of no great difficulty, whilst the efficiency of high-temperature smelting has increased hand in hand with the simplification of the operation.

DIAPHRAGMS AND CATAPHORESIS.

During the last few years the electrical properties of colloids have received ever-increasing attention by investigators in the subject of physical and electro-chemistry, which cannot fail to be reflected in the electro-chemical industry of the future. A discussion of the results already obtained lies somewhat outside the province of this volume,* but it may be remarked in passing that at the present time there are three distinct lines of research in this field which have already proved extremely helpful in the industry:—

1. The preparation of colloidal metals as sols in various

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* For further information on these subjects, the reader is referred to: Svedberg, "Die Methoden zur Herstellung Kolloider Losungen." V. Weimarn, "Grundzuge der Dispersoid Chemie." Freundlich "Kapillarchemie." Donnan, Membrane equilibria, *Zeit. f. Elektrochemie*, **17**, 572, 1911.

dispersion media by the two methods, (*a*) cathodic dispersion, and (*b*) dispersion by means of an electric arc.

2. The use of protective colloids in the electrolytic deposition of metals.

3. The calculation of the drop of potential across diaphragms, and also the velocities of ionic migration through the pores of the materials used in electrolytic operations, where it is desirable to separate the anode and cathode compartments.

POWER.

The deciding factors in the choice of a suitable method for the preparation of any product on a manufacturing scale are generally exceedingly complicated, and the relative values of raw materials, energy, labour and transportation to market costs vary from country to country, and, indeed, from place to place. The ideal site for a factory in a given locality cannot be indicated on a map by a strictly scientific method, such as marking off the power source at a point A, raw material sources at B and C, the distribution centre at D, and calculating the position of the site. Practical experience has shown that the energy factor is all important, and that big industrial enterprises spring up round the power sources.

Industrial electro-chemistry requires its power in electrical form, and the values of energy in this form are the dominant factors for the formation of these industries. The two chief sources of power are water and coal, although solar radiant energy, gasified peat and turf, and various organic fermentation processes, are being utilized on an increasingly extensive scale. It has been frequently claimed that owing to the relative cheapness of water-produced electricity compared to coal, no electro-chemical industries in a coal-producing country can compete with countries rich in water power. Many figures given for the actual cost of a kilowatt year are fallacious, owing to the different conditions obtaining both in supply and consumption of the energy produced and delivered from a generating station.

If the current be used solely for heating, as is the case in many electro-thermal operations, then owing to the heavy outlay necessary to build a water-power generating plant, the electrical energy derived from water is roughly about ten times as expensive at the present time as the fuel energy in coal. If, however, electrical energy is required in both cases, the expense of converting fuel into electrical energy usually makes it the more expensive of the two.

The running expenses of the two plants are also widely different; the fixed cost in a fuel-driven generator may be taken at about half the total cost of production, whilst in a water-driven plant the fixed cost is practically the only one to be considered. In order to arrive at comparative figures, it must be remembered that the efficiency of water-driven plants has practically reached its upper limits, whilst the inflation by prospectors and real estate agents of the cost of possible water-power sites as well as the growing æsthetic public opinion against the destruction of nature's scenery, are all tending to elevate the water-produced power costs. On the other hand, the improvements in turbine-driven plant, gas firing, utilization of coal by-products, and the possible advent of the gas turbine may lower the cost of the fuel-produced electricity. At the present time electricity produced in an up-to-date generating station can compete quite favourably with water power in those areas which have developed large industries like Niagara, but cannot compete with the newer electrical countries, such as Norway, Alaska or Africa, where land and water costs are small. In these cases the cost of importing the raw materials and the export of the manufactured article bid fair to compensate for the cheaper power costs.

The general conditions necessary for bringing down the power costs to the minimum are common to both methods of production. Economy in the production of electricity depends entirely upon the continuity of production and consumption, *i.e.* the load factor. Many electricity generators try to sell their interpeak current at a low rate to flatten their production curve, whilst the power consumers in their turn desire cheap power but cannot afford to buy discontinuous current, which is liable to be cut off at any moment by the producers, except in special cases for electric furnace work. At the present moment the problem of linking up various power stations to avoid clashing of peak currents in the areas using electrical power is being considered, but its practical operation is one of considerable difficulty. Economy can only be effected by producers supplying a large amount of power to consumers at a steady rate, and the amount must be so great that the lighting and heating load for the labour in the industries must be but a small proportion of the total load. Under these conditions of production and consumption the problem of power transmission becomes important. The present tendency leans to high voltage transmission, using copper or aluminium lines.* The first attempts to transmit at 10,000 volts were made in 1891. In 1901 50,000 to 60,000 volts transmission lines were in operation, and at the present time 110,000 to 150,000 volt lines are constructed. By raising the voltage increased quantities of power can be transmitted for longer distances at minimum cost for the conductor. There are, however, limits both to the voltage employed and to the distance over which the power has to be transmitted. On raising the voltage, not only have we the same Joule (Watt loss) loss by heating on the line, but the corona loss (above 100,000 volts) increases rapidly. The critical voltage at which the corona loss commences depends on the temperature pressure and presence of dust or fog in the air, as well as the radius of the line conductors. The smaller the conductor, the earlier does this electric brush discharge commence. Again, with high voltage lines, the expense of substituting steel or ferro-concrete towers for wood pole lines, and the fitting of high voltage insulators, raises the cost of line construction.

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* Although the specific conductivity of aluminium is only one half that of copper, yet per unit of weight, aluminium is a better conductor. Metallic sodium protected by glass tubes has also been suggested as a possible conductor.

These factors, which are specially important in industrial areas where precautions have to be taken, must be considered when the question of installing a separate power plant or the transmission of power from some distant generating station is considered. In western America the limiting distance appears to be in the neighbourhood of 250 miles, and in the east about 150 miles. If the station is further away it then becomes more economical to instal one's own generating plant. In England, where the population is denser and the cost of transmission lines considerably enhanced, the economical distance of transmission would be still shorter.

The Interim Report on the Electric Power Supply in Great Britain, April 1917, points out the necessity for the development of very large power centres; the average of some 600 undertakings in Great Britain have power stations of 5000 h.p., or about one-fourth the capacity of one single generating machine of economical size, and about one-thirtieth of the size of what may be considered as an economical "power-station unit." Thirteen of such "super-power" stations are contemplated.

The present methods of power production can be divided into the following groups:—

1. Hydro-electric.
2. Coal.
3. Gas.
4. Oil.

Hydro-electric Power.—Water power is exceedingly scarce in Great Britain, the only large installation being at Kinlochleven, where about 20,000 kw. is developed for the production of aluminium; potential sites may be found both in Wales and Scotland. Within the Commonwealth there are several very large undeveloped power sources, notably in Ireland on the Erne and Shannon, in Canada, Egypt, India, South Africa, New Zealand and British Guiana. The cost of installation and running vary very considerably from country to country. The following figures may be taken as the approximate pre-war running costs :—

Place.	Total cost per kw. year to consumer.
Kinlochleven	45*s*. 8*d*.
Ontario, Canada	41*s*. 3*d*.
Hora-Hora, New Zealand	81*s*. 7*d*.
N. California, U.S.A.	68*s*. 3*d*.
Saulte-Ste. Marie, U.S.A.	54*s*. 6*d*.
Niagara, U.S.A. side	67*s*. 1*d*. to 112*s*. 8*d*.
Legnano, Italy	20*s*.
Turin, Italy	54*s*. 4*d*.
Briançon, France	18*s*. 2½*d*.

The Scandinavian development of water power during the last few years has been a remarkably large one. Very low figures are quoted for the cost at Odda and Svaelgfos in Norway and Trolhätten in Sweden, *e.g.* from 11*s*. to 12*s*. per kw. year. The actual selling costs of this power, when full running costs, depreciation, and Government royalties are included, are higher. The Norwegian and Swedish Governments seem to be of the opinion that the natural economic selling costs lie between 25*s*. and 40*s*. per kw. year.*

Although the figures cited above are subject to wide variations, the approximate figure of 40*s*. per kw. year may be taken as a fair average selling price, on a pre-war basis, for hydro-electric power, where the installation costs are not high.

As is naturally to be expected, the pre-war installation costs for hydro-electric power vary widely, depending on the size of the plant and the engineering difficulties associated with the erection. In the U.S.A. £26 seem to be taken as a conservative standard cost, whilst the Kinlochleven installation in Scotland is said to have cost £27 per kw. In Norway the installation costs average about £15 per kw., rising to over £20 per kw. in the later installations. The earlier plants were installed at a much cheaper rate, owing to the fact that a large choice of available sites was permissible.

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* *Norwegian Royal Commission*, Sept. 1915.

The feasibility of using tidal energy has been discussed from time to time. This potential source of energy suffers from the disadvantage that to ensure continuity of supply large reservoirs would have to be erected to deal with the periods of slack water.

Coal Power.—A pound of good quality coal will produce from 11,500 to 14,000 B.T.U., and the average may be taken as 13,000 B.T.U.s per pound; since a kw. hour is equivalent to 3415 B.T.U.s, an ideal engine should be able to produce 4 kw. hours of electrical energy per lb. of coal. The most efficient steam-driven generator at present existent is undoubtedly the turbo generator, which offers the additional advantages of having low maintenance changes, and can be constructed in large units at very cheap installation costs. For large turbo generators, units of 20,000 to 50,000 kw. capacity, which are considered to be the minimum sizes compatible with economic working efficiency, about 15,000 B.T.U.s would be required per kw. produced. Smaller plants at present in operation consume some 20,000 B.T.U.s per kw. hour. The thermodynamic efficiency of such a generating set would therefore be 22·7 per cent. The capital installation costs for the large units are estimated to lie between £11 and £13 per kw. installed, figures which compare extremely favourably with those cited for the hydro-electric power installations.

In 1915, 253,179,000 tons, and in 1916, 256,348,381 tons of coal were mined in Great Britain, of which about one-quarter left the country. It is evident that a slight export tax on such a valuable raw material would considerably lower the price for the home consumer. It is stated that* the average selling price of coal in 1914 was 9*s.* 11·79*d.*, and in 1915, 12*s.* 5·60*d.* per ton. It would, therefore, appear possible to deliver coal in bulk at the large power stations contemplated by the reconstruction committee at from 7*s.* 6*d.* to 10*s.* per ton. Taking 7*s.* 6*d.* as the minimum, we

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* "Mineral Production of the United Kingdom in 1915: Mines and Quarries." Pt. iii., c. 8444.

obtain the following minimum cost of production per kw. year :—

Coal	33s. 10d.
Running costs and depreciation=10 per cent. on Installation cost	21s.
Total ..	54s. 10d.

To produce 1 kw. year for 40s., the pre-war value of hydro-electric power, coal would have to be delivered at the power plant for 4s. 3d. per ton. Although the post-war price for hydro-electric power may be considerably higher than the pre-war rate, yet a still greater increase in the cost of raising steam must be expected. It is extremely probable, however, that the altogether disproportionate rise in the freight rates will be sufficient to swing the pendulum over to the side of those power installations which are situate close to their markets.

Gas Power.—The boiler efficiency of a plant where steam is raised by gas firing is some 5 per cent. better than where coal is employed, owing to the fact that in the one case the fuel is perfectly homogeneous, requiring a definite and fixed quantity of air for combustion, whilst in the case of coal firing, combustion proceeds in stages, necessitating a variable air supply; thus, liberation of unburnt fuel as smoke, with the deposition of partly carbonized tar on parts of the heating system, can scarcely be avoided. Apart from this consideration, the market value of the by-products obtained in the distillation of coal is greatly above their value as fuel suitable for raising steam, and it would appear economically sounder to recover these by-products even if their fuel value were lost to the power plant. This would naturally necessitate an increased coal consumption as far as electrical power production was concerned, but on the other hand countries with supplies of coal available would obtain large quantities of products useful as raw materials for their various industries.

The relative advantages and disadvantages of partial gasification of the coal at low or high temperatures, under a slight pressure or vacuum, lie outside the province of this book. It is evident, however, that the nature and amounts of the various by-products being dependent on the conditions of gasification, can be controlled so as to suit the conditions of the market for fertilizers, benzol, chemicals, metallurgical coke, power or illuminating gas. We will only consider the hypothetical case where the coal is practically completely gasified to produce gas, by-products and clinker in one operation by the suitable introduction of steam, which we will assume can be obtained as waste from the main generating plant.

The efficiency of a gas producer is in the neighbourhood of 70 per cent. One ton of coal, containing 30 million B.T.U.s., on complete gasification will give nearly 60,000 cubic feet of gas containing 21 million B.T.U.s.

We have further noted that 15,000 B.T.U.s are required for a coal-fired boiler to give 1 kw. hour; with a 5 per cent. better efficiency for gas firing, 14,250 B.T.U.s would be required. Hence for a kw. year, 5·96 tons of coal would be required With coal at 7*s*. 6*d*. per ton, a kw. year with a gas-fired turbo-generator would cost :—

For coal	44*s*. 8*d*.
For gasification	32*s*. 0*d*.
Running costs and depreciation ..	21*s*. 0*d*.
Total ..	97*s*. 8*d*.

or 42*s*. 10*d*. dearer than a coal-fired turbo-generator set.

Against this must be set the value of by-products obtained in gasification of coal, amongst which may be mentioned :—

	Present net * value.	
Rectified tar	41*s*. 7*d*.	(If sold as crude tar
Ammonium sulphate ..	8*s*. 10*d*.	20*s*. 9½*d*.)
Benzol	5*s*. 11½*d*.	
Sulphocyanide ..	1*s*. 3½*d*.	
Sulphuric acid ..	2*s*. 4½*d*.	
Pan coke and breeze ..	3*s*. 10*d*.	
Total ..	63*s*. 10½*d*.	

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* Net value represents possible profit on sale at current rates, after deducting working costs for recovery and making allowance for depreciation of any special machinery utilized.

Under these somewhat idealistic conditions the price of a kw. year would fall from 97*s*. 8*d*. by 63*s*. 10*d*.=33*s*. 10*d*., or 6*s*. 2*d*. below the average water-power costs. If large, installations were erected for the gasification of coal in connection with the turbo-generator stations contemplated, doubtless the price of by-products on the market would fall and the disparity between costs of the alternate methods of production would tend to disappear, but there can be no doubt as to which system would be most advantageous to the nation.

Gas Engines.—We have already noticed that to produce 1 kw. hour in a coal-fired turbo-generator, 15,000 B.T.U.s are required, which figure may be reduced to 14,250 B.T.U.s if gas firing is adopted. In a good modern large gas engine only 13,500 B.T.U.s would be necessary to produce 1 kw. hour. In addition, by the use of the heat from the exhaust, steam can be raised to run a subsidiary plant. The exhaust heat of 13,500 B.T.U.s of gas exploded in the gas engine will raise steam equivalent to 3,500 B.T.U.s. In other words, the net energy consumption per kw. hour is only 10,000 B.T.U.s. In spite of the apparent advantages in the use of a more efficient prime mover, the limitations in size, 3000 kw. units being the largest constructed, together with the heavy installation expenses, make the working costs and depreciation on machinery more than counterbalance any fuel economy which is to be obtained.

The natural solution for power generation by means of gas is the realization of that long-sought machine, the gas turbine.

Power-gas sources are to be found in peat, turf, natural oil, gas wells, and in various fermentation industries, such as in the production of acetone, the retting of flax, and the hydrolysis of sewage in septic tanks.

Oil Engines.—The Diesel oil engines are the most efficient prime movers in technical operation, the B.T.U. consumption per kw. hour being only some 8,500. For relatively small electro-chemical installations, a Diesel engine operating on a low grade oil or gas-works tar would present several advantages.

THE METALLIFEROUS RESOURCES OF THE BRITISH COMMONWEALTH

In subsequent sections of this volume a short description is given of the various electrolytic and electro-thermal methods employed for the isolation of the metals and the production of metallic alloys and compounds. We have already indicated that in the British Commonwealth, including England, there exist the potential sources of large quantities of electrical energy, capable of being produced at low rates. For the successful development of a thriving electro-chemical industry, a few conditions only need be observed. Firstly, the necessary enterprise of financiers and manufacturers; secondly, the development of the educational system so as to ensure the supply of specialists trained in the branches of electro and physical chemistry, without which knowledge no old process can be economically modified, or new one developed, so as to compete in the open market with the highly organized foreign undertakings. The third important factor, viz. the availability of cheap electric power, has already been discussed. We have still to consider the possible lack of raw material for those industries which we must create to ensure our economic stability. The errors committed before the war, typified by such glaring examples as allowing the control over the Broken Hill Australian zinc ores and the Brazilian and Travançore Monazite sand deposits to be taken over by Germany, will probably not be repeated. On the other hand, other nations, profiting by these examples, will become more appreciative of the value of their own deposits, and the supply of raw materials from foreign countries will be partly, if not entirely, replaced by offers to supply manufactured goods. We shall, therefore, be compelled to return to our natural resources, if, indeed, our national spirit has not been sufficiently aroused by recent events, so that we shall prefer to develop our own resources even if foreign offers appear more advantageous.

The location of deposits of metalliferous ores within the

British Commonwealth given below are drawn from the last Report of the Advisory Council to the Department of Scientific and Industrial Research,* and a paper by C. Cullis to the Society of Engineers.† It will be noted that the supplies at present available and capable of being developed at some future date are by no means inconsiderable, and if stock of the world's ore deposits could be taken, it is probable that the greater portion of the metalliferous ores, with some few exceptions, would be found to be located within this area.

Iron.—The quantity of iron ore smelted in the United Kingdom in 1913 was 24 million tons, of which 8 million tons were imported. Large deposits of iron ores are found in the following countries :—

Great Britain.—Hematite, magnetite and ironstone in many counties.

Scotland.—Ironstone in Ayr, Dumbarton, Fife, Lanark, Linlithgow, Midlothian, Renfrew and Stirling.

Ireland.—Ferriferous bauxite in County Antrim. Hematite in County Down, County Wicklow, Cork, Clare, Longford and Leitrim.

Newfoundland.—Hematite on Bell Island.

Canada.—Hematite in Nova Scotia, Ontario and the Yukon. Magnetite in New Brunswick, Quebec and British Columbia.

India.—Hematite and ironstones in the Bengal Presidency and the Central Provinces. Magnetite in the Madras Presidency.

South Africa.—Siliceous hematite in W. Griqualand and Bechuanaland. Siliceous magnetite in the regions round Pretoria. Low-grade ore is stated to be plentiful in Rhodesia.

Australia.—Hematite in South Australia, New South Wales, Victoria, and parts of Western Australia and Queensland. Iron ore in Western Australia, a few miles north of Perth.

Tasmania.—Magnetite, estimated at 25 million tons, is stated to be available.

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* Published May 1917.

† *Trans. Soc. Eng.*, Dec. 1916, p. 25.

New Zealand.—The Parapara deposits of limestone and the magnetite deposits at New Plymouth are reported to be extensive.

Chromium.—The chief exporters of chromite within the British Commonwealth, according to the most recent returns, were :—

Country.	Date.	Metric tons.
Rhodesia	1913 ..	63,384
Canada	1915 ..	11,486
India	1914 ..	5,888
Australia	1915 ..	638

Deposits also occur in Scotland, the Transvaal, Newfoundland and New Zealand.

Cobalt.—Up to 1904, New Caledonia supplied 90 per cent. of the world's output. In that year the development of the Ontario silver cobalt nickel mines began, and these have now obtained the monopoly in the production of cobalt. The Commonwealth producers of cobalt ore are :—

Country.	Date.	Metric tons.
Canada	1914 ..	401
N. S. Wales	1910 ..	10

Other sources of supply may be found in India at Jaipur and in the Balmoral district of the Transvaal.

Manganese.—According to the Home Office statistics, the production of manganese ores was :—

Country.	Date.	Metric tons.
United Kingdom ..	1915 ..	4,640
India	1914 ..	693,824
Canada	1915 ..	47
Queensland	1915 ..	203

Extensive deposits are also found in Egypt, New Zealand, Newfoundland, Cape Colony and the Gold Coast.

Molybdenum.—The following was the world's production of molybdenite in 1915 :—

Country.	Metric tons.
N. S. Wales	35
Queensland	99
Canada	128

Molybdenum is also found in England, Scotland and India.

Nickel.—The production of nickel ore is practically confined to the extensive Cobalt and Sudbury deposits of Ontario. In 1915 the amount of nickel ore mined in this area was over 1,300,000 tons. Other deposits in Canada are said to exist, notably in Northern Alberta. Nickel has also been reported to be present in deposits in East Griqualand, S. Africa.

Titanium.—Deposits of rutile and titaniferous iron ore are found near Quebec, Canada ; New South Wales and near Adelaide, S. Australia, as well as in New Zealand, but up to the present time have not been developed.

Tungsten.—The production of tungsten ores within the Commonwealth during 1914–1915 was as follows :—

Country.	Metric tons.
United Kingdom	329
Burma	2,326
Malay States	291
Canada	15
Queensland	663
N. S. Wales	83
Victoria (1913)	50
New Zealand (1913)	231
Tasmania (1913)	58

Deposits which have not yet been worked are found at Rajputana in India, and on the Subti river in Rhodesia. Before the war over one-half of the world's tungsten ore consumption was mined within the Commonwealth, yet no ferro-tungsten and but a very small quantity of metallic tungsten was manufactured in England. Ferro-tungsten is now produced at Widnes, Luton and Sheffield, in England, for the English Steel Industry.

Vanadium.—Small deposits of mottramite (Pb and Cu Vanadate) have been observed in England in Cheshire, Wiltshire and Shropshire, but appear to be too small to be worked on a commercial scale. It is stated that Broken Hill, Rhodesia, may prove to be a useful source of vanadinite, whilst smaller quantities are found in Western Australia.

Zirconium.—In the form of zircon, large quantities are available in the heavy sea sands of S. India and Ceylon. As sylenite, it occurs in several localities in Scotland, Ireland, Australia and Canada, but none of these sources have been developed.

Copper.—In 1912, the world's copper consumption was just over one million tons, of which Great Britain and the Dominions provided one-tenth. 80 per cent. of the British production is obtained from Queensland and New South Wales, where in 1913 an output of nearly 50,000 tons of metal was reached. Extensive deposits have been worked in British Columbia and Ontario, whilst in South Africa, the Cape Province, the Transvaal and Rhodesia offer fields for further development. Chalcopyrite deposits are found in Cornwall, Devon and N. Wales, and cupriferous pyrites in Co. Wicklow, Ireland. It is stated that the deposits in British New Guinea are to be developed on a large scale.

Lead and Zinc.—The world's lead production just before the war exceeded 1,000,000 tons, and the zinc consumption was much of the same order. In 1912, 25,500 tons of lead ore and 11,700 tons of zinc ore were mined in the British Isles, chiefly in Wales and W. England, and this was exported for reduction. The chief source of lead and zinc ores before the war was the Broken Hill area in New South Wales, where 500,000 tons of ore, consisting of galena blende mixtures containing pyrites with a gangue of garnet quartz and rhodanite, were annually exported. Other Australian deposits are found in W. Australia, Queensland, Tasmania and New Zealand.

The chief lead and zinc ore producing area in Canada is the Koolenay district, British Columbia, where over 86,000 tons of lead ore and 11,000 tons of zinc ore were raised in 1913.

It is claimed, according to prospectors, that the Rhodesian Broken Hill deposits in North West Rhodesia exceed those in Australia, and are capable of extensive development.

Deposits are also formed in Upper Burma, where the mines were worked at a very early date by the Chinese for silver.

Tin.—The world's tin consumption is stated to be about 130,000 tons, of which the Malay States provide over 50,000. In Cornwall, where tin has been mined for a very great number of years, the annual production is still 5,000 tons, and capable of further development and improvement.

Tin ores are also found in Burma, and less abundantly in Australia, Tasmania, New South Wales and Western Australia. In Africa a development of the Nigerian deposits is to be expected.

Aluminium.—There is a marked scarcity of bauxite deposits within the Commonwealth. Since the annual world consumption of aluminium is in the neighbourhood of 100,000 tons, and is rapidly rising, it is unfortunate that our sole deposit is found in the Co. Antrim, Ireland, where the annual output is equivalent to only 1,500 tons of metal.

Other sources from which the metal can be economically obtained must be sought for, and production from these alternative ores encouraged.

In India, British Guinea and the Malay States, extensive deposits of laterite, a low grade bauxite rich in iron, appear capable of economic development, whilst alunite, a hydrated potassium aluminium sulphate, is found in New South Wales, in India, and on Vancouver Island in Canada.

The possible utilization of the felspars must also be considered as a future source of this metal.

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SECTION I.—ELECTROLYSIS IN AQUEOUS SOLUTIONS

COPPER.

THE electrolytic refining of copper is by far the oldest and largest of electrometallurgical processes, and has had a remarkable development especially in America, where over 85 per cent. of the world's copper production is dealt with. Of recent years some advance has been made on the electrolytic recovery of copper directly from the ore by leaching with a suitable solvent and subsequent electrodeposition of the metal.

The Electrolytic Recovery of Copper from its Ores.—Early experiments such as those of Marchese and Nicolajew, made on coarse metal matte (Cu_2S,Fe_2S_3) and white metal matte (Cu_2S) obtained in the ordinary metallurgical process, indicated that these sulphides, although easily cast into anodes and of sufficient electrical conductivity for use in electrolytic cells, using copper and ferric sulphate containing free sulphuric acid as electrolyte, were unsuitable for this purpose owing to the rapid accumulation of impurities in the electrolyte and the uneven solution of the anodes. The liberation of sulphur—

$$Cu_2S \rightarrow CuS' + C\ddot{u} \rightarrow C\ddot{u} + S''$$

which adhered to the anode caused the voltage to rise above economical pressures, whilst only low current densities could be used, 0·3 amp. per 100 sq. cms.

Borchers in 1908 conducted some experiments[1] at Mansfield, in which the matte was further refined by blowing in a Bessemer converter, then fusing the Cu_2S now free from the metalloids into anodes. An acid copper sulphate electrolyte was used, and with a current density of 0·5 amp. per 100 sq. cms. good deposits of pure copper were obtained. Agitation of the electrolyte was found necessary to detach the sulphur deposit from the anodes. For a short period over 10 tons of copper were produced per week by this method.

Attention was then directed to the method of leaching out the copper from the crude ore or from concentrates. Subsequent electrolytic deposition of the metal from the electrolyte with insoluble anodes was employed, and the spent electrolyte could then be returned to the leaching vats.

(a) *The Ferric Sulphate Process.*

This method, originally suggested by Siemens-Halske, utilized ferric sulphate as a solvent.

Oxidized copper ores such as the oxide or carbonate can be crushed and leached directly. Sulphide ores containing iron pyrites are roasted at a low temperature to convert the iron sulphides into ferric oxide. The original idea was to roast at such a temperature as to leave the copper sulphide unchanged, but in practice the temperature had to be elevated to 450° to 480° C. to ensure complete conversion of the iron sulphide; at this temperature most of the copper is also oxidized. Dead roasting is to be avoided owing to the possible formation of insoluble copper silicates and iron copper oxide complexes as well as the possible loss of silver. Leaching with a 2 to 7 per cent. solution of ferric sulphate is conducted in wooden vats, and solution of the copper takes place according to the following equations :—

$$(1)\quad Cu_2S+Fe_2(SO_4)_3=CuSO_4+2FeSO_4+CuS$$

$$(2)\quad 2CuS+2Fe_2(SO_4)_3+3O_2+2H_2O=2CuSO_4+4FeSO_4+2H_2SO_4$$

$$(3)\quad Cu_2S+2Fe_2(SO_4)_3=2CuSO_4+4FeSO_4+S$$

$$(4)\quad 3Cu_2O+Fe_2(SO_4)_3=3CuSO_4+Fe_2O_3.$$

The ferric sulphate solution is produced by the atmospheric oxidation of scrap iron dissolved in sulphuric acid.

This process has been experimented with at the Ray Mines, Arizona, at Cananea, and in a modified form at Rio Tinto, Spain.

With ores containing 3 per cent. to 1·9 per cent. copper, over 80 per cent. extraction can be obtained. Electrolysis is conducted in a divided cell using thin sheet copper cathodes. The problem of a suitable anode material for use in sulphate baths has not yet been satisfactorily solved. Platinum is ruled out on account of cost. Carbon and graphatized carbon, although satisfactory in chloride electrolytes, are rapidly destroyed by the oxygen evolution occurring in sulphate solutions. Lead peroxide sheets (formed *in situ* from lead sheet) have been successfully used, and on account of their low cost are used for most technical operations. Manganese oxide and fused magnetite (Fe_3O_4) electrodes are on the whole more satisfactory than lead, but more expensive.

As diaphragm for dividing the anode compartments from the cathode, millboard asbestos is generally used.

Vertical electrodes are usually employed, although horizontal ones have been suggested.

The cells are arranged in series, and the copper sulphate-ferrous sulphate solution flows through the cathode compartments and returns through the anode chambers. Owing to the deposition of copper on the cathodes during the flow the electrolyte becomes specifically lighter, and consequently enters each cathode chamber at the base and leaves by the top. The reverse flow takes place in the anode compartment (Fig. 1).

The ferrous sulphate produced from the interaction of Cu_2S and Cu_2O on ferric sulphate serves to depolarize the anode according to the equations —

$$\begin{array}{ll} \text{Cathode :} & CuSO_4 \rightarrow \ddot{Cu} + SO_4'' \\ & \qquad\quad \downarrow \\ \text{Anode :} & SO''_4 + 2FeSO_4 \rightarrow Fe_2(SO_4)_3 \end{array}$$

instead of the evolution of oxygen according to the equation—

$$2SO''_4 + 2H_2O \rightarrow 2H_2SO_4 + O_2$$

The saving in the electrical energy required to bring about the deposition of copper from a copper sulphate solution with an anode depolarizer is very great and can be calculated as follows :—

The minimum decomposition voltage of copper sulphate with the deposition of copper at one electrode and the liberation of oxygen under atmospheric pressure and with no overvoltage at the other, can be calculated from the thermal data of the reaction

$$2CuSO_4+2H_2O\rightarrow 2\overset{\uparrow}{Cu}+H_2SO_4+\overset{\uparrow}{O_2}$$

requiring 56,300 calories per gramme atom of copper.

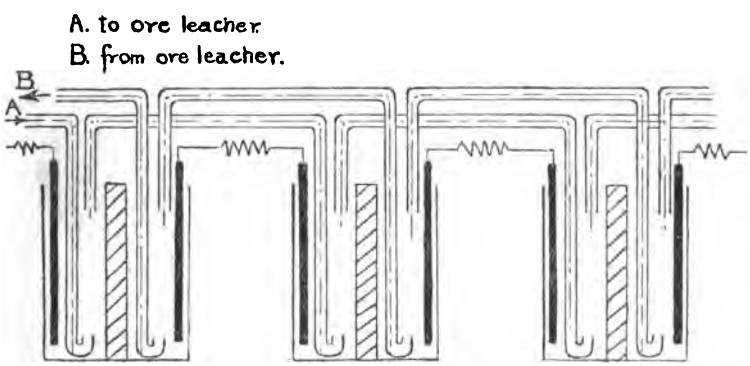


FIG. 1.—Arrangement of circulation in cells for deposition of copper from cupric ferrous sulphate electrolytes.

A. Cathode compartment. B. Anode compartment.

The theoretical decomposition voltage is therefore

$$\frac{56{,}300 \times 4{\cdot}2}{96{,}540 \times 2} = 1{\cdot}22 \text{ volts.}$$

With ferrous sulphate as anodic depolarizer we have the equation

$$CuSO_4+2FeSO_4\rightarrow Cu+Fe_2(SO_4)_3$$

requiring only 16,800 calories ; hence the requisite decomposition voltage is

$$\frac{16{,}800 \times 4{\cdot}2}{96{,}540 \times 2} = 0{\cdot}36 \text{ volt.}$$

The introduction of a diaphragm into the cell, however, necessitates the use of a much greater externally impressed electromotive force. In the experimental runs, between 0·8 and 1·8 volts were used with a current density of 0·2 amp. per sq. dcm.

(b) *The Sulphuric Acid Process.*

The use of sulphuric acid as a leaching agent for copper ores has advanced more rapidly than the ferric sulphate process, and may be said to have outgrown the experimental stage.

As in the ferric sulphate method oxidized ores can be leached without any treatment, but sulphide ores first must be roasted.

At the Chuquecamata mine in Chile, a large plant is in the course of erection with a capacity of 335,000 pounds of copper per day extracted from 10,000 tons of ore containing brochantite (an oxy-sulphate of copper) averaging about 2 per cent. copper. It is proposed to crush the ore to pass a 0·25″ mesh, to leach it with approximately 12 per cent. sulphuric acid in concrete leaching vats lined with mastic asphalt. It was found that the solution would be efficiently filtered through cocoanut matting set between wooden planks. C. Smith [2] gives the following analysis of the resulting electrolyte :—

	gms. per litre.
Cu	50·44
Fe	3·71
Mn	0·07
P	0·06
As	Nil
Sb	Nil
CaO	0·80
MgO	3·32
Al_2O_3	1·61
Na_2O	21·60
K_2O	5·00
SO_3	122·75
Cl	11·52
Free acid as H_2SO_4	28·00
Solids on ignition	189·40
HNO_3	4·0

It will be noted that both arsenic and antimony are absent, both being very deleterious for copper deposition (see p. 40).

The main objectionable impurity is the chloride, since not only is part of the chlorine evolved at the anode during electrolysis, but part is included in the deposited copper as cuprous chloride ; it was therefore proposed to remove the chlorides previous to electrolysis. This was effected by agitating the solution with shot copper in revolving drums. Cuprous chloride is formed according to the equation

$$2CuCl_2+2Cu\rightarrow 2Cu_2Cl_2$$

which can be filtered off, dried, fused with calcium chloride, and reduced to metallic copper by smelting with coke. It is proposed to use magnetite anodes 4 feet long, 5 inches wide and 2 inches thick, with five to a vat, and the ordinary sheet electrolytic copper anodes, 3 feet wide and 4 feet deep. The spent electrolyte in the experimental plant contained 1·5 per cent. copper, and was returned at this stage to the leaching vats. The average extraction was found to be close on 91 per cent.

Laszczynski[3] obtained an efficiency of over 91 per cent. with a current density of 0·5 to 1 amp. per sq. dcm., with an electrolyte containing 3 per cent. of copper, obtained by this leaching process.

At Butte Montana a 2 per cent. carbonate ore is treated by leaching with 10 per cent. sulphuric acid after crushing to $\frac{1}{2}''$. Previous to electrolysis the electrolyte is heated by steam to 60° C. At a neighbouring plant electrolysis proceeds with an agitated electrolyte using 1·4 amps. per sq. dcm.

Ricketts[4] cites a case of effective leaching with sulphuric acid on an oxidized carbonate ore at Ajo, Arizona, the ore being crushed to $\frac{1}{4}''$; subsequent electrolysis using composite coke-lead anodes gave a yield of 1 lb. of copper per kw. hour (63·5 gms. per 0·08 kw. hr.).

(c) *The Sulphate Process, using Sulphur Dioxide as a Depolarizer.*

Occasionally sulphur dioxide is injected into the anode chamber of a divided cell to act as depolarizer, or the sulphur dioxide may be made to agitate the liquid round the anode, as suggested by Carmichael, in a simple cell. Hard rubber tubes are most effective for conducting the SO_2 into the electrolyte.

Sulphur dioxide is a more powerful oxygen depolarizer than ferrous sulphate; the critical decomposition voltage for copper sulphate solution in a cell anodically depolarized with SO_2 is given from the thermochemical data—

$$CuSO_4+SO_2+2H_2O \rightarrow Cu+2H_2SO_4$$

with the evolution of 7,300 calories, or the theoretical voltage is

$$\frac{-7300 \times 4{\cdot}2}{96{,}540 \times 2} = -0{\cdot}15 \text{ volt.}$$

In other words, SO_2 should be able to precipitate copper from a copper sulphate solution without the aid of any electrical energy. This is actually the case, and forms the basis of the Neill and Van Arsdale processes developed by Weidlein and others for leaching and depositing from solutions. The cycle of operations claimed for these processes is given in the following equation :—

$$CuO+SO_2=CuSO_3$$

Cupric sulphite is soluble in excess of sulphurous acid; on driving off the excess of sulphurous acid the cupric sulphite is not deposited, but a red precipitate, $Cu_2SO_3.CuSO_3$, is formed. The cuprous cupric sulphite on heating under pressure with sulphuric acid precipitates copper according to the equation—

$$Cu_2SO_3.CuSO_3+2H_2SO_4=Cu+2CuSO_4+2SO_2+2H_2O$$

The cupric sulphate can similarly be converted into metallic copper by the addition of sulphur dioxide and the intermediary precipitation of the double sulphite.

In practice anodic depolarization is not complete, usually only about 60 per cent.[5] and applied voltages from 0·2 to 1·5 volts have been used.

At the International Copper Company's plant in Canada, lead anodes separated 1½ inches from sheet copper cathodes are used with a copper content of 2·5 per cent. and 2·5 per cent. sulphuric acid in the electrolyte. The applied voltage is 1·5 to pass 0·7 ampere per sq. dcm. with a current efficiency of 90 per cent.

(d) *Chloride Processes.*

The original chloride process is that detailed by Hoepfner at work in Silesia. The finely crushed ore is leached with a cupric chloride solution containing sodium or calcium chloride heated to about 70° C. in wooden drums. Lead chloride would be removed on cooling, and the metalloids and iron by lime. Owing to the presence of excess chlorine ions the small amount of copper going into solution as cuprous chloride becomes complex :

$$\dot{\mathrm{Cu}}+2\mathrm{Cl}'\rightleftarrows\mathrm{CuCl}'_2$$

thus permitting of the preparation of relatively concentrated solutions of copper in the cuprous state. The electrolyzer consists of a series of divided cells with asbestos parchment or perforated mica diaphragms. Carbon or graphitized carbon can be used as anode material in chloride solutions, although Hoepfner found these not sufficiently refractory, and suggested the use of ferrosilicon. Sheet copper cathodes are employed. In the cathode and anode compartments the following reactions take place :—

$$\text{Cathode : } \mathrm{Cu_2Cl_2} \rightarrow \overset{\uparrow}{\mathrm{Cu}}+\mathrm{CuCl_2}$$
$$\text{Anode : } \mathrm{Cu_2Cl_2}+2\mathrm{Cl.}'\rightarrow 2\mathrm{CuCl_2}$$

the cuprous chloride in the electrolyte acting as an anodic depolarizer for the liberated chlorine. The catholyte and anolyte consisting chiefly of cupric chloride, after passing through the cells, are mixed and returned to the leaching plant.

The theoretical decomposition voltage obtained from the thermochemical data—

$$2\mathrm{Cu}+\mathrm{Cl_2}=\mathrm{Cu_2Cl_2}+35{,}000 \text{ calories,}$$

is as follows :—

$$\frac{35{,}000 \times 4{\cdot}2}{96{,}540} = 1{\cdot}53 \text{ volts,}$$

the copper in this case being monovalent. The electrical energy required to deposit a gramme molecule (63·5 gms. of metal), viz. 96,540 × 1·53 watt secs. = 0·043 kw. hour.

If cupric chloride were used as electrolyte the decomposition voltage would be—

$$\begin{aligned} Cu + Cl_2 &= CuCl_2 + 62{,}500 \text{ calories} \\ &= \frac{62{,}500 \times 4 \cdot 2}{96{,}540 \times 2} \text{ volts} \\ &= 1 \cdot 35 \text{ volts,} \end{aligned}$$

the copper in this case being divalent. The electrical energy required to deposit a gramme molecule (63·5 gms. of metal) being 96,540 × 2 × 1·35 watt secs. = 0·075 kw. hour.

There is, therefore, a distinct advantage in using cuprous chloride instead of cupric chloride as electrolyte, although since the decomposition voltage of the cuprous salt is higher than that of the cupric, the energy gain is not quite that to be expected by a change from the divalent to the monovalent state of the metallic ion, viz. double the output per kw. hour.

The further advantage of anodic depolarization can be calculated from the heat of reaction—

$$Cu + CuCl_2 = Cu_2Cl_2 + 19{,}400 \text{ calories}$$

The theoretical voltage is therefore

$$\frac{19{,}400 \times 4 \cdot 2}{96{,}540} = 0 \cdot 84 \text{ volt,}$$

or the minimum energy required to deposit a gramme molecule (63·5 gms. of the metal) is 96,540 × 0·84 watt secs. or 0·022 kw. hour. The actual voltage required was said to be 0·6 to 0·8 volt per cell. Early experiments in Saxony (1892) proved unsuccessful, chiefly owing to difficulty of leaching with cupric chloride according to the following equation :—

$$2CuCl_2 + Cu_2S = 2Cu_2Cl_2 + S$$

Further investigation has shown that cupric sodium chloride solution is a good leach for certain oxidized ores such as $CuSiO_3$ found at Miami, Arizona, where a 2-hours' leach with a 5 per cent. cupric chloride solution on a 3 to 5 per cent. copper ore ground to pass a 60-mesh sieve yielded a 99 per cent. extraction.

At a current density of 1·1 to 1·3 amps per sq. dcm., 1·0 volt was required per cell. Greenawalt has used an acid chloride leach with success, using SO_2 as acid. He finds it desirable to roast ores containing much iron or sulphides. A divided cell is not used in his process, and with an applied voltage of 1·53 volts copper can be deposited with an electrical energy expenditure of 0·080 kw. hour per gramme molecule (63·5 gms.) of copper.

Leaching with ferric chloride was the subject of a Belgian patent (the Body process). The ferrous chloride formed during the leaching acts as an anodic depolarizer, according to the equation—

$$2FeCl_2+Cl_2=2FeCl_3$$

The theoretical voltage can be calculated from the heat of reaction—

$$Cu+2FeCl_3=CuCl_2+2FeCl_2+7000 \text{ calories };$$

therefore, the minimum theoretical E.M.F. required

$$=\frac{7000 \times 4{\cdot}2}{96{,}540 \times 2}=0{\cdot}15 \text{ volt.}$$

The Electrolytic Refining of Copper.—The raw material for electro-refining is blister copper, obtained from the ordinary smelting process. The metal analyzes some 98 per cent. copper, and is cast into bars some 3 feet long, 1·5 feet wide and 0·75 inch thick, and occasionally larger, to serve as soluble anodes. Pure electrolytic copper sheet is used as cathode material. The anodes and cathodes are suspended alternately in wooden bitumastic or lead-lined vats carefully insulated from the ground, some 2 inches apart, although with care the distance between the electrodes can be reduced to as little as ·5 inch, connected to copper bars which alternate from tank to tank. About thirty pairs of electrodes are used in each tank.

With a current density of from 1·1 to 2·2 amperes per square dcm., the voltage loss per bath is approximately 0·2 to 0·4 volt. A number of tanks are connected in series sufficient to make up a 100 or 200 volt circuit. With a current consumption of 2·2 amps. per sq. dcm. of cathode surface and with 30 cathodes each of 100 sq. dcm. (3×1·5 ×2 sq. ft.) a total current of over 5000 amps. per tank is required. The modern tendency is to make the electrode surface large and the tanks larger; currents up to 15,000 amperes have been proposed. The average consumption of current per pound of copper deposited is 0·166 kw. hour, the ampere efficiency being 90 per cent. The electrolyte consists essentially of an acid copper sulphate solution containing 5 to 10 per cent. free sulphuric acid and 10 to 15 per cent. copper sulphate which is continually circulated from tank to tank to avoid stratification. The electrodes are removed every three or four weeks. Since copper is being dissolved at one electrode and deposited on the other, theoretically no E.M.F. should be necessary to transfer the copper, but, as has been already pointed out, a small P.D. must always be applied to the electrodes, amounting to from 0·2 to 0·4 volt. Sixty per cent. of the fall in potential across the bus bars falls on the ohmic resistance of the electrolyte. In consequence the electrolyte in copper refining gets warm owing to the energy absorbed, 60 per cent. of 0·3 volt×5000 amperes=900 watts per cell in the above-mentioned case. Cooling by radiation normally balances the heat energy supplied when the temperature has risen to about 35 C., but owing to the high temperature coefficient of the electrolyte it has been found economical

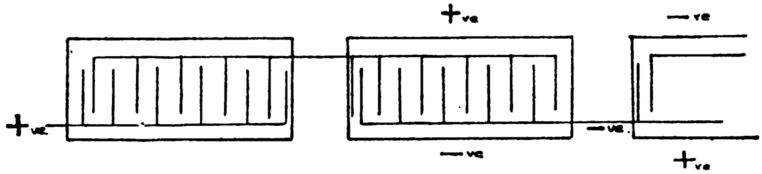


FIG. 2.—General arrangement of electrolytic cells with plates in parallel.

to still further heat it to about 55° C. with exhaust steam.

An alternative electrode arrangement has been adopted in some plants. The anode and cathode are end electrodes in each vat, and the intermediate electrodes are bipolar, copper being dissolved off one side and deposited on the opposing face of the next electrode. The bipolar electrodes are removed and the electrolytic deposit stripped off. When the electrolyte becomes too contaminated for further use the copper sulphate is partly removed by crystallization and completely by the addition of scrap iron.

The Impurities present in Electrolytic Copper.—Blister copper may vary widely in composition according to the nature of the ore and the materials used in the smelting process. Its copper content may fall as low as 91 per cent. or rise to over 98 per cent. The following analyses indicate the usual impurities present and their amounts:—

	1	2[1]	3
Copper	91·00	94·06	98·224
Arsenic	1·20	4·36	0·94
Antimony ..		0·57	0·40
Bismuth ..	1·15	0·02	0·04
Carbon	0·70	—	—
Iron	1·10	0·03[2]	trace
Lead	1·16	0·13	0·02
Nickel	1·14	0·37	0·28
Silver	1·09	—	30 oz. per ton
Gold	—	—	$\frac{1}{10}$ oz. per ton
Zinc	1·17	—	—
Sulphur ..	—	0·37	0·03
Oxygen ..	0·29	0·10	0·05

The impurities in electrolytic copper should not exceed 0·12 per cent. It is evident that it is more economical to pay special attention to the preparation of high grade raw blister copper than to attempt the electrolytic purification of low grade anodes when such a high grade of purity is demanded and can be obtained.

The impurities in refined copper may be due to a variety of causes,[7] such as (1) the inclusion of the electrolyte between the growing crystals on the cathode surface ; (2) electrolytic deposition ; (3) mechanical contamination from the slimes. These impurities adversely affect the quality of the deposited copper by making it brittle and of low electrical conductivity, or valuable by-products such as gold or more rarely platinum and palladium may be removed in the cathode.

During the disintegration of the raw copper anode the impurities in the copper either go into solution or fall to the bottom as slimes. The impurities in solution may become deposited in the cathode copper either by direct mechanical occlusion or by electrolytic deposition whilst the slimes become occluded by mechanical means.

Gold and silver are entirely eliminated as anode slimes, none is found in solution. It is found that increasing current density causes an increase in the gold and silver loss in the cathode; this phenomenon is attributed to the greater agitation of the electrolyte with the use of high current densities increasing the quantity of suspended or "float" slimes. Arsenic is present both in the slimes and in the electrolyte ; it is probably deposited only by mechanical occlusion of the electrolyte, since the quantity of arsenic deposited varies only with the concentration of arsenic in the electrolyte and is not affected by increased current density.

Nickel which forms a continued mixture of solid solutions with copper (Fig. 3) is probably electrically deposited, since the difference of potential between the electrodes, viz. 0·4 volt, would be sufficient to electrolytically deposit a solid solution of copper and nickel containing very little nickel. The decomposition potential of nickel sulphate is much higher than that of copper, but the E.M.F. generated between copper and copper nickel alloy containing but little nickel can be made infinitely small. Oxygen is generally present in deposited copper either as occluded gas or as cuprous oxide in solid solution. It is still a matter of speculation as to the relative importance of these three factors, viz. electrodeposition, inclusion of electrolyte and inclusion of slime, on the amount and nature of the impurities in the deposited copper. Generally it may be stated that an increase of contamination with increasing current density and applied voltage points to slime inclusion or electrolytic deposition, whilst increasing contamination with increasing electrolytic contamination points only to electrolytic inclusion.

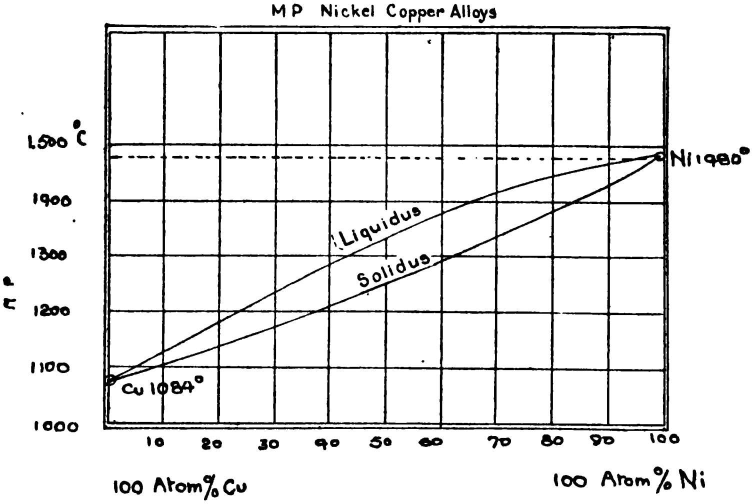


FIG. 3.—Freezing-melting-point curves of nickel-copper alloys.

Electroplating with Copper.—In electroplating with copper, pure electrolytic copper is usually employed as anode material; consequently, although no trouble is occasioned by the presence of impurities in the metal or the electrolyte, more attention has to be paid to the conditions necessary for obtaining uniform, even, and compact deposits of electrolytic copper.

The practice of violent agitation of the electrolyte or movement of the cathode, *e.g.* for electrotype rolls, rotation at a high speed is used to a greater extent than in copper refining. Various electrolytic compositions are in use, and the current density is usually less than that employed in refining processes.

The two most important electrolytes used for this work are the acid sulphate and the cyanide bath.

Copper Sulphate Electrolytes.—Copper sulphate electrolytes may vary in composition from a 5 per cent. copper sulphate pentahydrate content to a saturated solution with the addition of from 0 to 10 per cent. of free sulphuric acid.

The current density usually employed varies from 1·5 to 2·5 amperes per square decimetre, although with high rotational speeds for the cathode as suggested by S. Cowper Coles up to 40 amperes per square decimetre can be employed. The addition of iron salts to the electrolyte has frequently been advocated. Mechanical burnishers such as agate used by Elmore, sheepskin by Dumoulin, and glass beads by Consiglio are frequently employed in addition to either agitating the electrolyte or rotating the cathode.

Cyanide Solutions.—Copper plating is frequently used for coating iron or steel as an intermediary film for nickel plating. A thin film of copper can be deposited on the iron by simple immersion of the iron in an acid copper sulphate solution. Iron is more electropositive than copper, and as has already been described the conditions necessary for the deposition of one metal by another are directly obtained by the application of Nernst's hypothesis of electrolytic solution pressures to metals.

If E_{Fe} and E_{Cu} be the electrolytic solution pressures of the iron and copper respectively, and $C_{F\ddot{e}}$, $C_{C\ddot{u}}$, be the concentration of ferrous iron and cuprion in the solution, copper will be deposited at the expense of iron going into solution, as long as

$$\frac{E_{Fe}}{C_{F\ddot{e}}} > \frac{E_{Cu}}{C_{C\ddot{u}}}$$

and the driving force or E.M.F. of the system will be

$$\frac{RT}{2F} \log \frac{E_{Fe}}{C_{F\ddot{e}}} - \frac{RT}{2F} \log \frac{E_{Cu}}{C_{C\ddot{u}}}$$

The iron is, however, quickly entirely coated and deposition ceases. In practice, however, "flashing" is liable to give a porous and spongy deposit, and other electrolytes have to be chosen. The choice of an electrolyte is limited to one in which the E.M.F. of the hypothetical equation—

$$\text{E.M.F.} = \frac{RT}{2F} \log \frac{E_{Fe}}{C_{F\ddot{e}}} - \frac{RT}{2F} \log \frac{E_{Cu}}{C_{Cu}}$$

is reduced to zero or is practically negligible, *i.e.* copper must exhibit no tendency to be deposited at the expense of the iron. This can be obtained by the use of an alkaline electrolyte. In these solutions the concentration of cuprion is depressed, making the right-hand term of the above equation greater, and the iron is rendered passive, *i.e.* its apparent electrolytic solution pressure $E_{F\hat{e}}$ is lowered. The metal becomes more noble or less easily attacked.

The following are some typical examples of such solutions :—

(i) *Copper salts and Cyanide.*

Copper carbonate	100 gms./litre.
Potassium cyanide	200 gms./litre.

U.S. patent 129,124 describes a mixture—

Copper sulphate	100 gms.
Copper acetate	200 gms.
Potassium cyanide	150 gms.
Potassium carbonate	150 gms.

made up with 1 litre of water.

(ii) *Copper salts, ammonia, and Cyanides.*—Cowper Coles describes the following solution as most effective :—

Copper sulphate	36 gms.
Ammonia (·880)	26 gms.
Water	182 c.c.

mixed with—

Potassium cyanide	38 gms.
Water	148 c.c.

The solutions are mixed and made up to one litre. Electrolysis is conducted with a current density of 0·4 to 0·5 ampere per sq. dcm.

Watt recommends the following solution :—

Copper sulphate	230 gms.
Water	1 litre.

to which ammonia (·880) is added until the precipitate is just redissolved. To this solution a strong solution of potassium cyanide is added until the blue of the cuprammonium cyanide is just changed to the lilac of the cuprocyanide complex. Electrolysis is best conducted at 60° C.

(iii) *Copper salts, Bisulphite, and Cyanides.*—Baths containing bisulphite have been recommended by Pfanhauser and others. As typical of this class two may be mentioned—

(*a*)	Na_2SO_4	200 gms.
	$NaHSO_3$	200 gms.
	Copper potassium cyanide	300 gms.
	Ammonia soda	100 gms.
	KCN	10 gms.
	Water	10 litres.
(*b*)	$NaHSO_3$	10 gms.
	Na_2CO_3	40 gms.
	Water	1 litre

mixed with—

$Cu(CH_3COO)_2$	40 gms.
NH_4OH (·880)	14 gms.

with the addition of—

70 per cent. KCN	56 gms.
Water	1 litre.

Alkaline cyanide baths containing both tartrates and thiosulphates have also been used with success. Other alkaline baths which do not contain cyanide usually make use of the solubility of copper tartrate in caustic soda. Oxalate baths containing copper and ammonium oxalate with free oxalic acid have been suggested by Classen, Gauduin and others.

The Conditions necessary for Uniform Distribution of Copper.—We have already tabulated the various types of electrolytes used in the electrodeposition of copper, and have briefly referred to the practice of agitating the electrolyte or rotating the cathode; the exact mechanism by which the cupric or cuprous ion is finally deposited out of solution on the cathode, building up a solid coherent mass of metal, is not yet clear, but the following considerations go far to justify the combined use of many of the old recipes and customs founded on experience or accidental discoveries, and serve to sift out the worthless from an already extensive list.

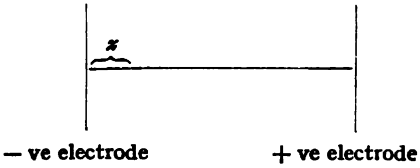
The Influence of Cathode Rotation or Electrolytic Agitation on the Nature of the Deposit.—If two unattackable electrodes, *e.g.* platinum, be immersed in a solution of any salt, say copper sulphate in water, and an externally impressed electromotive force be applied to the electrodes, no electrolytic decomposition will take place if the P.D. between the electrodes does not exceed the decomposition potential of the salt. Although no visible electrolysis will take place, a small current will be observed to flow. This "diffusion" current, owing to the different ionic mobilities of the cuprion and the sulphation, effects a difference in concentration between the solutions surrounding each electrode, as was first shown by Hittorf. After a short time dynamic equilibrium sets in when the rate at which the current tends to set up a difference in concentration is exactly balanced by the rate at which the diffusion compensates this change.

Sand[8] first pointed out the probable effect of raising the applied electromotive force above the decomposition potential of copper sulphate, but below that of sulphuric acid.

At the cathode copper is deposited and the thin film of electrolyte on the surface of the cathode has lost cuprion to an extent which can be calculated from the current passing through the cell. We have seen that the P.D. between a metal and its solution is given by the relation—

$$\text{E.M.F.} = \frac{RT}{2F} \log \frac{E_{\mathrm{C}\ddot{\mathrm{u}}}}{C_{\mathrm{C}\ddot{\mathrm{u}}}}$$

Consequently the back electromotive force of the cell would rise to the value of the impressed voltage if the further supply of copper ions to the electrolyte at the cathode surface was not supplied by diffusion and by the electrical migration of further cuprion—



Let C_0 be the concentration of the electrolyte at the commencement of electrolysis. After a time t the concentration at a point x distant from the electrode becomes C_x, and $\frac{dc}{dx}$ is the concentration gradient from the electrode.

The quantity of salt diffusing per unit time across unit area with a gradient $\frac{dc}{dx}$ is given by the equation—

$$Q = D\frac{dc}{dx}$$

where D is the diffusion constant. When $t=0$, $C=C_0$ between $x=0$ and $x=\infty$; according to Fick's law the rate at which the concentration alters is given by the equation—

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2}$$

or, on integration—

$$C_x = C_0 - \frac{Q}{\sqrt{\pi D}} \cdot \int_0^t \frac{dt}{\sqrt{t}} \cdot e^{\frac{-x^2}{4Dt}}$$

At the electrode itself, the concentration after a time interval t becomes—

$$(1)\quad C = C_0 - 2Q\sqrt{\frac{t}{\pi D}} = C_0 - 1{\cdot}1284Q\sqrt{\frac{t}{D}}$$

The quantity of copper sulphate which has to be supplied by diffusion (Q) is equal to the difference between that deposited and that supplied by the ionic migration, or

$$Q = \frac{i}{96{,}540} - \frac{n_c i}{96{,}540} \text{ gm. equivalents,}$$

where i is the current in amperes and n_c the migration constant of the cupric ion.

Substituting the value of Q in the above equation, we obtain—

$$(2)\quad C = C_0 - \frac{1{\cdot}1284}{96{,}540}\, i(1 - n_c)\sqrt{\frac{t}{D}}$$

or, when $C=0$, *i.e.* at the moment when no cupric ions are present in the layer of elctrolyte near to the electrode—

$$C_0 = \frac{1{\cdot}1284}{96{,}540}\, i(1 - n_c)\sqrt{\frac{t}{D}}$$

or—

$$t = \frac{C_0^2 D}{(1 - n_c)^2 i^2}\left(\frac{96{,}540}{1{\cdot}1284}\right)^2$$

When this time t has passed, further electrolysis can only proceed by the discharge of hydrion at the electrode at the higher potential difference necessary to decompose sulphuric acid which is present in the electrolyte.

It is evident that under equilibrium conditions the period of uniform deposition can be prolonged by starting with a large value for C_0, the initial concentration, a high diffusion constant and a high migration constant, which last two factors can be sensibly increased by elevating the temperature.

For the investigation on the beneficial effect of stirring we can adopt the hypothesis of Noyes and Whitney [9] and of Nernst,[10] applied to the solution of a solute in a solvent. A solid in the course of solution, in their view, is to be regarded as surrounded by a thin film of saturated solution whence the salt diffuses into the less concentrated solution, and the rate of solution is governed by the rate of passage of salt from the saturated to the unsaturated solution.

If δ be the thickness of the saturated film, then A the solution constant per unit area is given by

$$A = \frac{D}{\delta}$$

According to Noyes and Whitney, when the rate of solution is $\frac{dc}{dt}$

$$\frac{dc}{dt} = A(C_{sat.} - C)$$
$$= \frac{D}{\delta}(C_{sat.} - C)$$

where $C_{sat.}$ is the saturation concentration and C the concentration of the surrounding solvent.

Applying this equation to the case of deposition under consideration—

$$\frac{dc}{dt} = \frac{D}{\delta}(C_0 - C)$$

where C_0 is the initial concentration of the solvent and C the concentration at the electrode. But $\frac{dc}{dt}$, the rate of deposition, is equal to Q, where—

$$Q = \frac{i(1 - n_c)}{96{,}540}$$

or

$$Q = \frac{D}{\delta}(C_0 - C)$$

or

$$C_0 - C = \frac{Q\delta}{D} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

We have seen, however, that when no rotation or movement of the electrolyte is considered, from equation (1)—

$$C_0 - C = 2Q\sqrt{\frac{t}{\pi D}}$$

$$Q\frac{\delta}{D} = 2Q\sqrt{\frac{t}{\pi D}}$$

or

$$t = \frac{\delta^2\pi}{4D}$$

From this equation the conclusion can be drawn that up to a time $t = \frac{\delta^2\pi}{4D}$ electrolysis can be continued with the same current efficiency either with or without stirring the electrolyte.

By rapid rotation of the electrode or agitation of the electrolyte, the film thickness can be decreased and the period of efficient deposition increased. A. Fischer[11] has calculated from this equation the influence of rotation on δ, the film thickness in the case of a solution of copper sulphate with the following results :—

Revolutions per minute of stirrer.	Film thickness.
250	0·0635 mm.
800	0·0565 „
1100	0·0510 „

Thus, apart from the advantage to be derived from a mechanical burnishing of the deposited metal by the circulating electrolyte a distinct economy in time of deposition by the use of higher current densities is effected.

The Influence of Simple or Complex Electrolytes on the Nature of Deposit.—From the preceding considerations we have noted that the electromotive force between the copper and the surrounding electrolyte given by the equation E.M.F. $= \frac{RT}{2F} \log \frac{C_{Cu}}{C_{Ca}}$ is not constant, but may vary in a marked manner quite close to the electrode due to the impoverishment of the electrolyte in cupric ions by electrodeposition. The advantage of supplementing the supply of cupric ions normally migrating to the cathode by agitation when high current densities have to be employed is thus at once apparent, but the influence of the concentration of the cupric ion in the solution on the nature of the deposit is by no means so clear. Since high current densities and economical energy consumption are always desirable, at first sight it might seem advantageous to lower the E.M.F. between electrode and solution by increasing the concentration of cupric ions. In practice, however, for electroplating and electro-analysis, where a fine hard coherent deposit is desired, quite the converse has been found to hold; namely, that a high cuprion concentration round the electrode is not advisable in spite of the fact that impoverishment may take place; even if it occurs so rapidly that, unless agitation be adopted, too low a concentration is arrived at.

We must assume that to obtain a hard deposit similar to a worked metal we have to supply the extra energy required to work the metal or burnish it electrically. In other words, a limiting value is set to the term $\frac{RT}{2F} \log \frac{E_{Cu}}{C_{Cu}}$ below which, although the metal is deposited, the deposit occurs in a non-compact form. It must not be forgotten, however, that if the term $E = \frac{RT}{2F} \log \frac{E_{Cu}}{C_{Cu}}$ be made too great by the depression of the cuprion concentration, disturbances may occur due to the simultaneous deposition of other ions, since the P.D. between solution and metal may exceed the critical P.D. necessary to deposit the other cation. The compactness of the deposited metal may be attributed to the high potential gradient under which the ion is deposited on the metal, or, on the other hand, to the rapidity with which the ion changes into the metallic form and loses its charge and water of hydration associated with it, according to the following scheme :—

$$\begin{array}{c} C\ddot{u}(H_2O)_n \rightarrow Cu(H_2O)_n \rightarrow Cu \\ \qquad\qquad + 2\oplus \end{array}$$

There is strong evidence that the ions are hydrated in solution, but we are not yet certain whether the loss of the hydration water proceeds as rapidly as the loss of electric charge.

Since in complex ion electrolytes the concentration of the metallic ions is so low, the view is frequently held that the electrolytic deposition of the metal is not a simple direct discharge of the metallic ion as has been suggested, but a secondary effect due to the discharge of other ions.

For example, in potassium cuprocyanide, an anion complex, the following equilibria are undoubtedly present:—

$$K_2Cu_2(CN)_4 \rightleftarrows 2K^{\cdot}+2Cu(CN)'_2$$
$$Cu(CN)'_2 \rightleftarrows C\dot{u}+2(CN)'$$
$$KCN \rightleftarrows K^{\cdot}+(CN)'$$

The value of

$$E=\frac{RT}{F}\log\frac{E_{Cu}}{C_{C\dot{u}}}=-0{\cdot}658 \text{ volt.}$$

We obtain for a normal solution of cuprous salt and the observed potential difference a concentration of cuproions of $10^{-30}n$. If cupric ions are assumed to be present, the value of—

$$E=\frac{RT}{2F}\log\frac{E_{Cu}}{C_{C\ddot{u}}}=-0{\cdot}329 \text{ volt,}$$

which represents a concentration of $10^{-48}n$. cupric ions.

In the case of the copper ammonia or cupramine complex as cation—

$$Cu(NH_3)^{\cdot\cdot}_4 \rightleftarrows C\ddot{u}+4(NH_3)$$

A normal solution of cupric ions is reduced to $10^{-9}n$. by the formation of the cupramine complex, the P.D. rising from —0·329 to —0·0694 volt between metal and solution.

With these very small metal ion concentrations and high electrolyte-electrode potential differences the discharge of potassium ions, where the necessary P.D.

$$E=\frac{RT}{F}\log\frac{E_K}{C_{K^{\cdot}}}$$

must rise to +3·20 volts for a normal potassium ion solution, may possibly take place under working conditions; the potassium then secondarily deposits copper from the solution according to the equation—

$$2K+K_2Cu_2(CN)_4=2Cu+4KCN$$

Since equally good results are obtained with complex metal electrolytes whether the metallic complex is an anion or cation, Daniel's view [12] that the migration of the complex away from the cathode at points of highest current density results in an automatic readjustment of the current distribution can scarcely be correct.

The Influence of Various Addition Agents on the Deposit.—In the previous section it has been pointed out that in all probability the nature of the deposited copper is greatly influenced by the conditions under which the discharge of the cupric ion is brought about, the diagrammatic scheme being—

$$\ddot{\mathrm{Cu}}(\mathrm{H_2O})_n \rightarrow \mathrm{Cu}(\mathrm{H_2O})_n \rightarrow \mathrm{Cu} + 2\oplus$$

When the potential difference between solution and electrode is great the cupric ion is discharged with great speed at the electrode surface and the labile intermediate complex has but a short existence. We can likewise influence this process of cathodic discharge not only by a variation in the potential difference, but by influencing the stability of the unstable metal hydrate which is a hypothetical intermediary in the deposition. The nature of the deposited copper can be made to vary so as to suit the purpose for which it is intended. In electro-refining a tolerable uniformity of surface and density will suffice; in electroplating smoothness and hardness are desirable; in electroanalysis great smoothness and hardness are necessary; and for special work such as wire or tube construction ductility is necessary.

The Use of Colloids in Copper Deposition.—Varying the stability of the intermediary phase directly influences the crystal size. The general practice is to add colloidal substances to the electrolyte, when the following conditions have to be observed. In acid solutions the added colloid must be positively charged, *i.e.* it must tend to be codeposited with the copper by electric endosmosis; gelatine, glue and tannic acid are colloids of this type. One part of glue in 1000 of acid copper sulphate electrolyte will give a fine-grained tenacious deposit under the usual conditions of electrolysis. The effect is more marked if the electrolyte be slightly warmed to 25°–35° C. Such colloids act as protective colloids to the labile metal hydrate and prevent the formation of loose honeycomb structures or large crystals. As has been pointed out by Bancroft,[13] the addition of colloids tends to decrease the crystal size.

A second class of addition agent is to be found in the form of salts which form insoluble colloidal hydrated hydroxides in neutral and slightly alkaline solution, *e.g.* tin and aluminium, and to a less extent, iron. In this case the colloid is actually formed in the electrolyte round the cathode, which tends to become alkaline during prolonged electrolysis with indifferent agitation.

Successful experiments have also been made with non-colloidal addition substances, both reducing and oxidizing agents.

The Use of Reducing Agents in Copper Deposition.—The deposition of copper is always attended with an electrical energy loss due to the following reaction taking place between the cathode material and the electrolyte. A similar attack on the copper anode also occurs:

$$\mathrm{Cu+CuSO_4 \rightleftarrows Cu_2SO_4}$$

$$\text{or} \quad \mathrm{Cu+C\ddot{u} \rightleftarrows 2C\dot{u}}$$

As indicated by the arrows, the reaction is reversible, and a rise in temperature shifts the equilibrium over to the right-hand side of the equation. The small quantity of cuprous ions which is present in solution tends to oxidize on exposure to air in the acid electrolyte according to the equation—

$$\mathrm{2Cu_2SO_4+2H_2SO_4+O_2=4CuSO_4+2H_2O}$$

The deposited copper can thus return again to its original state in solution in the electrolyte. Since a very high temperature or an electrolyte too concentrated in cupric ions favours the formation of cuprous ions, these extremes are to be avoided in copper deposition.

Reducing agents such as alcohol (3 to 5 per cent. in the acid electrolyte), sugar, molasses, hydroxylamine and pyrogallol have all been used. In pyrogallol and sugar solutions, not only does the reducing power limit the influence of the course of the reaction mentioned above, but sufficient colloidal material is usually present to act as a protective colloid.

The use of small quantities of chlorides up to ·004 per cent. have frequently been advocated; not only does it limit the concentration of the silver, antimony and bismuth in the electrolyte (by the limited solubility of the chlorides and oxychlorides formed), but it appears to be beneficial to the smoothness of the deposit; the cuprous ions present at the cathode will undoubtedly partially react with the chloride to form the complex $\dot{\mathrm{Cu}} + 2\mathrm{Cl}' \rightleftarrows \mathrm{CuCl}'$. Deposition of the cuprous ions will therefore take place from this complex instead of from the simple ionized salt.

The Use of Oxidizing Agents in Copper Depositions.—The use of oxidizing agents, usually nitric acid, is practically confined to the electroanalysis of copper. We have already noticed that under certain conditions of low cupric ion concentration in sulphate electrolysis and high current density, the difference of potential between electrode and solution $E = \frac{RT}{2F} \log \frac{E_{\mathrm{Cu}}}{C_{\ddot{\mathrm{Cu}}}}$ may rise to such a point that it approaches the potential difference required for evolution of hydrogen. The rapid evolution of hydrogen causes the deposited copper to assume a brown spongy appearance, which has been attributed to the formation of an unstable copper hydride or copper hydrogen solution. Nitric acid acts as a cathodic depolarizer for the hydrogen, being reduced to ammonia.[14]

The Electrodeposition of Bronze and Brasses.—Electrolytic depositions of "bronze" have been made, both as true bronzes, namely alloys of copper and tin, and also of brass or copper-zinc alloys. Nickel has also been substituted for tin or zinc, and even arsenic has been used to obtain a bronze-coloured deposit. The demand for bronze deposits has been chiefly regulated rather by their colour and appearance than by their actual composition.

The potential difference between a metal and a solution containing its ions is given by the equation—

$$E=\frac{RT}{nF}\log\frac{Em}{Cm}$$

where Em=the electrolytic solution pressure of the metal, and Cm the concentration of the n valent metallic ions in the solution. For the simultaneous deposition of two metals from an electrolyte containing both metals as ions the following relation must hold :—

$$\frac{RT}{n_1F}\log\frac{Em_1}{Cm_1}=\frac{RT}{n_2F}\log\frac{Em_2}{Cm_2}$$

or

$$\frac{n_1}{n_2}\log\frac{Cm_1}{Cm_2}=\log\frac{Em_1}{Em_2}$$

The following are the equilibrium potential differences between metals and solutions containing the metallic ions in normal concentration, taking the value

$$E=\frac{RT}{F}\log\frac{\text{P. hydrogen at 1 atmosphere}}{\text{normal H ion solution}}$$

as zero :—

Copper	—0·329 volt	(divalent ions only)
Zinc	+0·770 ,,	
Tin	+0·192 ,,	(divalent ions only)
Nickel	+0·228 ,,	

Advantage is taken of the fact that the complexity of the cuprous cyanide ion is much greater than that of zinc, nickel or tin complex cyanides, and it is thus possible to raise the deposition potential difference for copper to that point where the other metal also begins to be deposited.

The degree of dissociation of the various complexes varies with the temperature, and by electrodeposition from a mixed complex electrolyte at various temperatures it is possible to deposit either one metallic constituent or a series of alloys.

The variation of the complexity is given by the cathode potential at the various temperatures, and a few typical examples are shown in the following curves :—

It will be noted that there is a very marked dependence of the cathode potential on the current density. In these cases since the ionic concentration of the metals in the solutions is low and is removed rapidly by electrodeposition, we must assume that the rate of reformation of metallic ions by dissociation of the complex ion, *e.g.* $Cu(CN)'_2 \rightarrow 2CN' + C\dot{u}$ to arrive at equilibrium again is not instantaneous, but proceeds with a slow reaction speed. The speed depends in all probability on the complexity of the complex ion. It will be noted that the silver complex breaks down most rapidly, whilst the copper complex appears most stable.

The discharge potentials of the ions are of course measured against their respective metals; in the case of deposition on to an alloy partial depolarization of the less noble ion by the more noble constituent in the alloy will take place, thus tending again to lower the divergence between the two discharge potentials.

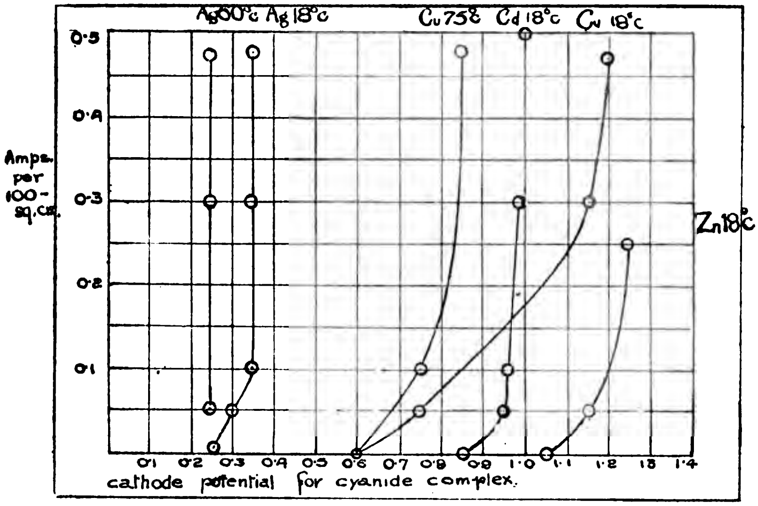


FIG. 4.—Influence of current density on the cathode potentials of cyanide electrolytes.

In the practice of alloy deposition we can control the nature of the deposit by the following independent variables:—

(1) The complexity of the electrolyte affecting the ratio $\frac{C\ \text{metal}\ (1)}{C\ \text{metal}\ (2)}$.

(2) The temperature affecting (1) and (3).

(3) The current densities affecting the velocities of reactions $\frac{\text{complex}\rightarrow\text{ion (1)}}{\text{complex}\rightarrow\text{ion (2)}}$.

(4) The composition of the deposit.

The following examples indicate some of the solutions where the deposition potential of the two metallic ions is the same :—

Copper-zinc.

(1)	Copper sulphate	25 gms.
	Zinc sulphate	29 gms.
	Potassium cyanide to dissolve the precipitate.	
	Water	1 litre.
(2)	Copper acetate	4·5 gms.
	Zinc sulphate	9·0 gms.
	Potassium hydroxide	67·0 gms.
	Potassium cyanide	7·5 gms.
	Ammonia (·880 sp. gr.)	30·0 gms.
	Water	1 litre.

Copper-tin.

(1)	Cuprous chloride	1·5 gms.
	Stannous chloride	1·2 gms.
	Potassium cyanide	10·0 gms.
	Potassium carbonate	100·0 gms.
	Water	1 litre.
(2)	Copper phosphate Sodium pyrophosphate	saturated solution.
	Sodium pyrophosphate Stannous chloride	,, ,,

added to—

	Sodium pyrophosphate	50 gms.
	Water	1 litre.
(3)	Copper sulphate	70 gms.
	Stannic chloride	8 gms.
	Potassium hydroxide	a small amount.
	Water	1 litre.
(4)	Copper sulphate	15·0 gms.
	Stannous oxalate	4·2 gms.
	Ammonium oxalate	55·0 gms.
	Oxalic acid	5·0 gms.
	Water	1 litre.

ZINC.

The conditions obtaining for the economical electrolytic recovery and refining of zinc are somewhat different from those for copper.

The recovery of copper from its ores by purely thermal processes is very economical, and it is only of recent years that electrolytic methods have appeared feasible. In the case of zinc, however, the recovery of the metal from the ore, or more generally from the roasted ore, is one of great difficulty. Not only are the retorts in which the reduction takes place according to the equation

$$C+ZnO=Zn+CO$$

very fragile, owing to the extremely high temperature necessary to bring about the distillation (over 1200° C.), but the condensation of the zinc vapour into a regulus cannot be accomplished without the loss of blue powder (see p. 142).

Successful attempts have been made to use internal electric heating for the reduction and distillation of the zinc; these will be dealt with in a later section.

With these disadvantages against reduction by means of carbon, early attempts were made to utilize electrolytic methods which may eventually entirely replace the early thermal processes.

In the problem of electro-refining of zinc the case is not comparable to that of copper. Not only is the demand for very pure zinc limited except for shell manufacture, where absolute uniformity in brass is necessary, but also the purification of zinc by redistillation *in vacuo* of the crude zinc obtained in the Belgian fuel furnaces is easily accomplished on account of the low boiling-point of the metal. The cost of electrolytic refining of zinc is higher than that of copper for reasons which will be stated. Thus the field for electrolytic purification of zinc metal will probably always be a limited one, but undoubtedly useful for working up certain technical by-products, such as galvanizer's dross (averaging 90 per cent. zinc and containing iron, tin and lead) and zinc scum from the Parkes lead desilverizing process (averaging 50 per cent. zinc and containing copper, lead, silver and any gold that may be present). The aluminium amalgam modification of the Parkes process yields a scum richer in zinc (70 to 80 per cent.). It is also extremely probable that the " blue powder " consisting chiefly of zinc and zinc oxide, being the uncondensed portion of the zinc regulus from the zinc furnace, could be more economically disposed of electrolytically than by briquetting with carbon and returning it in the furnace. With the growth of the electric furnace production of zinc the quantity of " blue powder " available for some such wet process will be extremely large.

The Electrolytic Recovery of Zinc.—As in the case of copper, many early attempts were made to use zinc ores and roasted ores briquetted with coke as soluble anodes in electrolytic cells, but were all unsuccessful.

Sulphuric Acid Processes.—Previous to the outbreak of war, Germany controlled the greater part of the zinc ore supply of the world mined in the Broken Hill area in Australia. Their control was enforced by acquiring the rights over the various flotation processes in operation to concentrate the ore before shipping to Europe. This ore is now available for the English market, and consists of sulphides of zinc, lead, a little silver and gangue, being essentially a blende galena complex.

The basis of all the sulphate electrolyte processes is the primary roasting at a low red heat to convert the sulphides into sulphates and oxides. The oxidized ore is then leached with dilute sulphuric acid and submitted to preliminary purification before electrolysis.

The earliest electrolytic sulphate process was devised by Siemens Halske and Laszczynski in Poland. Ten per cent. sulphuric acid was used as a leaching agent. Lead and most of the silver are removed as sulphate by filtration. Small quantities of other metals, such as iron and copper and soluble silica, are removed by fractional neutralization with lime, followed by filtration. The presence of iron in the ferric state is ensured by the addition of a little bleaching powder. Frequently a final agitation with zinc oxide or zinc dust is used before filtration. A nearly neutral solution of zinc sulphate is thus obtained, which is circulated through wooden electrolyzing vats containing sheet lead anodes and thin electrolytic zinc cathodes. With a P.D. of 3·8 volts per cell and a current density of 1 ampere per sq. dcm., 3·4 kw. hours will deposit 1 kgm. of zinc, showing a current efficiency of 80 per cent.

Modifications of this method are becoming increasingly important for the electrolytic recovery of zinc. The following difficulties were found to be inherent in the original process:—

Anode Material.—The adoption of lead as anode material was only made after extensive trials with other substances.

Carbon anodes, as has already been indicated, rapidly deteriorate under the action of the oxygen evolved at the anode. Early experiments by Ashcroft sought to eliminate the oxygen evolution by the use of a divided cell, using ferrous sulphate solution as a depolarizer, the ferrous sulphate being oxidized to ferric sulphate ; cathodic reduction of the ferric sulphate solution thus produced was accomplished after most of the zinc had been deposited. In this case ferric sulphate solution is used as leaching agent. Since complete anodic depolarization is not required, and cathodic reduction of the ferric sulphate proceeds practically quantitatively, the extra number of ampere hours required to reoxidize the ferrous sulphate was practically compensated for by the lower operating potential difference due to the anodic depolarization.

Soluble iron anodes were also used, but it was found in practice that the trouble associated with the use of diaphragms and the cost due to the loss of iron alone were sufficient to make the process impracticable. Lead anodes are now practically general, and usually prepared *in situ* from sheet lead, but as in the case of copper deposition carbon protected by a thick deposit of lead peroxide,[15] magnetite and manganese oxides have experimentally shown better results than lead sheet, so that there is reason to suppose that sheet lead will be finally eliminated as soon as the problems of uniformity of construction and low cost of manufacture have been solved.

The following table shows the excess voltage (or overpotential) over and above the actual decomposition voltage to be applied to ensure the liberation of oxygen at the anode :—

	Volts (overvoltage to oxygen).
Nickel	0·05
Iron	0·24
Lead peroxide	0·28
Platinum (black)	0·24
Platinum (bright)	0·44
Graphite	0·40

Cathode Material.—These are usually thin strip electrolytic zinc about $\frac{3}{16}''$ to $\frac{1}{4}''$ thick, separated by about 2″ from the lead anode. Difficulties are encountered in stripping the zinc deposit from the plate, and it is generally found necessary to form an artificial parting plane by slightly coating the electrode before use. (Dilute rubber solution, wax in alcohol, vaseline or glycerine are all effective.) Plates hard to strip frequently strip on warming, but a certain number have always to be melted up with the deposit.

A more serious difficulty is the corrosion occurring at the union of the zinc plate with the copper connection to the bus bar, and more especially at the surface of the electrolyte (Fig. 5).

At the line of contact between the zinc and the electrolyte aa′ the zinc is wetted with the spray, and since there is no applied E.M.F. to keep the zinc from solution in these acid drops, surface corrosion takes place. This is all the more violent owing to the greater acidity of the electrolyte near the surface; the zinc sulphate solution, being denser than the correspondingly concentrated sulphuric acid solution formed by the electrolysis, always tends to gravitate to the bottom of the electrolyzing vat and the acid to float to the top, unless prevented from doing so by active circulation. The corrosion is greatly assisted by the presence of atmospheric oxygen,[16] and plates may be eaten through in the course of a few hours. The usual method of prevention is by the use of pure zinc cathodes which are not readily attacked by acid, and if necessary by bitumastic paint to just below the line of the electrolyte. Recently, the use of aluminium plates as cathode material has been attended with unqualified success.

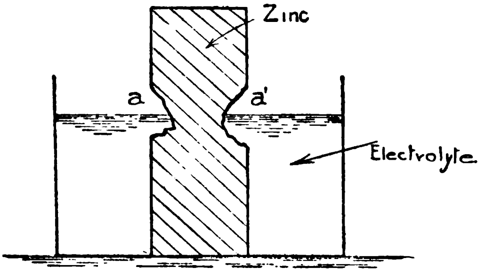


FIG. 5.—Surface corrosion of zinc cathode in zinc deposition.

Conditions for Deposition.—The conditions necessary for obtaining uniform deposits from a sulphate electrolyte have been the subject of many investigations, but the results obtained are conflicting. In the case of copper deposition the electrolytic potential of the metal E_{Cu} referred to the hydrogen electrode was $-0{\cdot}329$ volt; it is consequently easier to deposit copper from an acid copper sulphate solution than to liberate hydrogen. The electrolytic potential of zinc in a normal zinc ion solution is on the same scale $+0{\cdot}770$ volt. It follows that if hydrogen and zinc can be reversibly liberated or deposited at the anode of a cell in an electrolyte containing normal zinc ion and normal hydrion concentrations, hydrogen would be liberated before any zinc could be deposited, until an excess anodic potential of $+0{\cdot}770$ volt against the solution was applied above that necessary to liberate the gas. Mylius and Fromm[17] also experimentally arrived at the conclusion that a high concentration of zinc and a low acidity were most desirable in an electrolyte. Further, it was found necessary to work with a high current density.

The presence of basic salts is to be avoided owing to the formation of a spongy deposit, and in practice it is necessary to keep the electrolyte distinctly acid. The cause of spongy deposition has been shown definitely to be due to the presence of oxidizing impurities near the anode, and not to the formation of an unstable hydride of zinc, as was formerly considered.[18] Pring and Tainton [19] reinvestigated the problem, and were surprised to find that with strongly acid solutions and high current densities the deposition of zinc could be carried out with a high efficiency, especially after the addition of a small trace of colloidal material to the electrolyte. Their process is now the basis of several semi-technical deposition installations.

The electrolyte contains 150 gms. of sulphuric acid and 100 gms. of zinc sulphate per litre; perforated sheet lead anodes and zinc or aluminium cathodes. are used. The potential difference over each vat is about 5 volts, and the current density from 20 to 50 amperes per square decimetre. An efficiency of 95 per cent. can be obtained at a temperature of 18° to 25° C. The zinc deposited by this method from solutions containing manganese, lead, iron as grosser impurities and small traces of other substances usually obtained from roasted Broken Hill zinc concentrates, is remarkably pure, averaging well over 99·80 per cent.

The curve in Fig. 6 represents the results obtained by these authors, using 0·05 per cent. gum arabic as colloid in an electrolyte containing 13 to 14 per cent. zinc sulphate and 10 to 19 per cent. sulphuric acid with 0·1 per cent. of iron.

The explanation of these results where the ratio of the zinc deposited to the hydrogen liberated increases with rising hydrion concentration in the electrolyte is far from satisfactory.

As has already been pointed out in the introduction, the overpotential necessary for hydrogen liberation at a metallic surface varies with the nature of the metal. In the case of zinc an applied E.M.F. of 0·70 to 0·80 volt higher than the reversible decomposition potential of the acid must be applied to bring about the evolution of hydrogen. This excess over the theoretical raises the critical potential difference required to that necessary for the deposition of zinc, which in a normal zinc ion solution is +0·770 volt on the hydrogen scale. In the neighbourhood of the electrode under these conditions both ions are equally susceptible

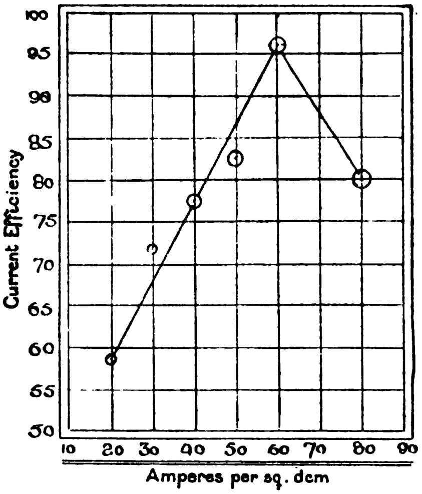


FIG. 6.—Influence of current density on efficiency in deposition of zinc.

to deposition, since the necessary deposition potential is practically the same. The zinc ions have, however, a natural preferment for deposition which may be explained on the assumption that the velocity of deposition according to some such scheme as follows :—

$$\left\{\begin{matrix}\mathrm{A}\\ \overset{\cdot\cdot}{\mathrm{Zn}}(\mathrm{H_2O})_n\end{matrix}\right\}\rightarrow\left\{\begin{matrix}\mathrm{B}\\ \mathrm{Zn}(\mathrm{H_2O})_n\end{matrix}\right\}\rightarrow\begin{matrix}\mathrm{C}\\ \mathrm{Zn}\end{matrix}$$

is greater than that of the hydrogen deposition, which may be depicted as

$$\left\{\begin{matrix}\mathrm{A}\\ 2\dot{\mathrm{H}}(\mathrm{H_2O})_x\end{matrix}\right\}\rightarrow\left\{\begin{matrix}\mathrm{B}\\ 2\mathrm{H}(\mathrm{H_2O})_x\end{matrix}\right\}\rightarrow\left\{\begin{matrix}\mathrm{C}\\ \mathrm{H_2}(\mathrm{H_2O})_x\end{matrix}\right\}\rightarrow\begin{matrix}\mathrm{D}\\ \mathrm{H_2}\end{matrix}$$

Not only have we other independent evidence that the hydration numbers *n* and *x* are not the same for both ions, but the second series of changes is bimolecular and not an intermolecular change like the first; both these factors probably greatly influence the velocity of conversion. Bennet and Thompson[20] believe that active hydrogen (H as distinguished from H_2 or $H^{\cdot}$) can deposit zinc from zinc sulphate solution. If this assumption be correct a secondary reaction between the hypothetical intermediary compound $2H(H_2O)_x$ and the zinc ions may occur according to the equation—

$$Z\ddot{n}+2H \rightarrow Zn+2\dot{H}$$

Many investigators have accepted modifications of this theory representing the change by the formation and decomposition of unstable hydrides. The advantage of a high current density is further emphasized by the consideration that the resolution of the deposited zinc proceeds at a constant rate for smooth deposits depending on the acidity of the electrolyte, thus by increasing the rate of deposition the apparent efficiency is also increased. Spongy surfaces will naturally dissolve quicker than smooth ones, owing to the greater area exposed to the solution.

The Use of Colloidal Addition Agents.—Pring and Tainton recommend the use of colloids to ensure the deposition of the zinc and to eliminate impurities which are likely to be deposited at a high working potential difference between the electrodes. This point has already been discussed in dealing with the deposition of copper. The usual colloids employed are dextrin, gum tragacanth and gum arabic of about 0·05 per cent. concentration.

Watts and Sharpe[21] suggest the use of 1 per cent. of eikonogen, pyrogallol or β-naphthol.

The Chloride Processes.—Hoepfner's original chloride process was developed and is still worked by Messrs. Brunner, Mond and Co., and is said to be at work at Duisberg and Fürfurt in Germany,[22] but the use of blende in preference to calamine as raw material has stimulated the employment of sulphate electrolytes, more than the chloride method.

A solution of zinc chloride is obtained by treating the roasted zinc ore with calcium chloride in a carbonating tower, when calcium carbonate is deposited according to the equation—

$$CaCl_2+ZnO+CO_2\rightarrow ZnCl_2+\underset{\downarrow}{CaCO_3}$$

Alternatively the ore can be given a chloridizing roast with salt. Iron and manganese are removed by the addition of bleaching powder and a little alkali whilst a final filtration over scrap zinc will deposit metals such as copper which may be present. A 10 per cent. solution of zinc as chloride is used as electrolyte, containing about 20 per cent. of sodium chloride, a little free hydrochloric acid (0·1 per cent.), and gypsum. According to Foerster and Günther, who carried out experiments similar to those of Mylius and Fromm on the sulphate solutions, the electrolyte must not be basic.

Operating with a diaphragm cell and a high current density 3 to 4 amperes per sq. dcm. at 3·5 to 7 volts per cell, good deposits of zinc analyzing 99·97 per cent. may be obtained provided that efficient circulation in the cathode compartment is maintained. The use of revolving cathodes possesses advantages for this process. The chlorine evolved from the anode compartment where carbon anodes are used can be used for preparing bleaching powder, for chlorination, or may be compressed and liquefied. The diaphragms are said to be of nitrated cellulose, but hydrated silica on asbestos fibre has been stated to give good results. It may be noted that the addition of colloidal addition agents is general practice. The cathodic current efficiency is stated to be well over 94 per cent., whilst at the anode only 85 per cent. efficiency is obtained on the chlorine actually collected.

The Electrolytic Refining of Zinc.—As has already been mentioned, except in certain cases for the utilization of by-products the method has but little commercial value.

Richards successfully used galvanizer's dross as anode material when cast with 0·1 per cent. aluminium. As electrolyte he used 15 per cent. zinc sulphate hydrate, 1·7 per cent. commercial acetic acid, and 0·8 per cent. sodium acetate. With zinc cathodes separated 4 cm. from the anodes and a current density of 1 ampere per sq. dcm. at a temperature of 30° to 32° C. and a voltage fall per cell of 1·25 volts, good deposits could be obtained provided that air agitation and good circulation were employed. The current efficiency varied between 80 and 100 per cent., and the average analysis showed only 0·05 per cent. impurity. The iron from the anode material was removed from the electrolyte by the air agitation, followed by filtration of the hydrated ferric hydroxide which was precipitated from the acetate solution.

The Gold and Silver Anstalt at Hamburg attempted the purification of the zinc scum obtained in the Parkes' lead desilvering process, containing from 50 to 70 per cent. lead, 10 to 50 per cent. zinc, and 5 per cent. copper, and frequently up to 7 per cent. of silver and a little gold, and 0·2 per cent. aluminium.

They employed a zinc sulphate solution and either cast anodes or granulated pieces lying on a horizontal carbon anode. With a current of 0·8 to 1 ampere per square dcm. and at 1·3 volts per cell good coherent deposits of zinc could be obtained, but the process did not prove commercially successful.

A chloride process using zinc and magnesium chlorides as electrolyte is said to be successful, in which the lead and silver chlorides deposited in the sludge can be cupelled to obtain the silver.

Electrogalvanizing.—Galvanizing is most commonly accomplished by the hot galvanizing process, namely, by cleaning the iron or steel plate, pickling it in acid, and dipping it in a bath of molten zinc at a temperature of about 450° C. A superficial alloy is made with pure zinc on the outside containing the compounds $FeZn_7$ and $FeZn_3$.

The formation of a film of iron-zinc alloy on the surface may considerably lower the breaking strain of the thin articles, such as hooks or cables, whilst the relatively high temperatures employed (450° C.) may cause a lowering in the tensile strength of steels due to this subsequent thermal treatment.[23] Under these circumstances electrodeposition from acid zinc sulphate electrolyte with lead peroxide anodes can be feasibly employed.

The necessary conditions for deposition are identical with those obtaining in the electrodeposition of zinc from sulphate solutions, and have already been referred to.

CADMIUM.

The electrochemical behaviour of cadmium is very similar to that of zinc. Its deposition from solution, however, does not present such great difficulties as the former metal, since its electrolytic potential on the hydrogen scale is only +0·420 volt, whilst zinc has a value of +0·770 volt. Thus though from a solution containing both cadmium and hydrogen ions hydrogen would be the first to be deposited, yet, as was the case with zinc, the overpotential of hydrogen against a cadmium cathode is very high, being +0·400 volt, making the conditions necessary for the deposition of the metal with a high current density practically identical with the former metal. Technically there is very little demand for the pure metal, and the electrolytic recovery and refining of the metal has not been accomplished on any scale; Brand[24] accomplished some large-scale experimental work on purifying cast anodes of the following composition, Cd 88·7 per cent., Zn 8·55 per cent., Pb 1·35 per cent., and Cu 1·35 per cent. As electrolyte he followed the usual practice of zinc refining, using a solution containing 10 per cent. cadmium as cadmium sulphate and 5 per cent. free sulphuric acid. His electrodes were spaced 5 cms. apart, and successful deposition was accomplished with a current density of 1·4 amps. per sq. dcm. The E.M.F. applied was at first practically zero owing to the presence of the highly electropositive zinc in the anode causing direct deposition of the cadmium. His final electromotive force was stated to be only 0·048 volt per cell.

Electroplating with cadmium has a small technical application. Under suitable conditions a soft white deposit may be obtained which after buffing takes on a high polish and resembles tin. Certain difficulties are inherent in electroplating articles with cadmium, which on deposition tends to develop a macrocrystalline structure, a serious defect when a smooth protective layer is desired. As in the case of copper, this tendency can be corrected either by the addition of suitable addition agents, usually colloidal, or by the adoption of a complex electrolyte. In practice, practically only complex electrolytes are employed. The usual electrolyte is the complex cyanide formed by solution of cadmium carbonate in a potassium cyanide solution. Russell and Woolrich,[25] Fischer,[26] and Basset [27] all give the composition of suitable plating baths. The electrolyte should contain from 1 per cent. to 4 per cent. cadmium in the form of cadmium carbonate dissolved in the minimum amount of potassium cyanide necessary, and subsequently 5 per cent. of potassium cyanide is added. Cadmium anodes are usually employed, and uniform deposition is obtained at a temperature of 40° C. with an applied E.M.F. of 3 volts.

GOLD.

The electrolytic deposition of gold has been utilized both as a means of obtaining the metal from a leaching solution which has treated the ore and for the purpose of plating less noble metals on an industrial scale.

The Electrolytic Recovery of Gold.—Gold generally occurs in the free state as veins running through the auriferous strata. When present in large quantities it can be separated from the crushed ore by repeated washing with water, the heavier gold particles being retained behind; frequently rough cloth or animal skins are used.

For poorer ores averaging only a few ounces to the ton, chemical extraction methods are employed. The earliest made use of mercury, as a solvent; the gold amalgamates with mercury, which is subsequently removed and the mercury recovered by distillation, leaving the gold.

There are several technical difficulties associated with the ordinary amalgamation process. The mercury occasionally "sickens" and becomes coated with a film of oxide, hindering its coalescence and tending both to lessen its power of amalgamation and to be carried away in the wash water. Electrolytic reduction of the mercury oxide by making it the cathode in an electrolytic cell or the addition of a small quantity of sodium rectifies the tendency. The gold itself may be coated with the oxide or sulphide of some other metal which may resist the amalgamating effect of the mercury. Two other solvents are also employed for the recovery of gold from its poorer ores, viz. free chlorine and potassium cyanide.

In the process of chlorine extraction the ore is finely crushed and extracted with an aqueous solution of chlorine water prepared from bleaching powder and sulphuric acid. This method of extraction is associated with the great disadvantage that other metals are dissolved in addition to the gold, and a very impure electrolyte results. More common practice is the extraction by means of potassium cyanide or potassium-sodium cyanide solution, in wooden tanks with continuous agitation by compressed air. The cyanide solutions possess the advantage that in dilute solution the solution of gold is comparatively rapid whilst other substances are relatively slowly attacked.

The dissolution of gold by potassium or sodium cyanide solutions requires the presence of oxygen or an oxidizing agent according to the equation[28]—

$$4Au+8KCN+2H_2O+O_2=4KAu(CN)_2+4KOH$$

Furthermore, the velocity of solution is greatly accelerated by the use of a slightly alkaline medium. The addition of sodium peroxide or potassium ferricyanide in small quantities is said to increase the rate of solution to four or five times the normal rate in the presence of air.

The Electrolytic Deposition of Gold from Leaching Solutions.—Deposition from a chloride or cyanide solution can of course be accomplished chemically. The zinc-lined boxes used for shipping the cyanide have been used for this purpose, whilst for the chloride solutions ferrous sulphate is generally employed. The Siemens-Halske process for the recovery of gold possesses several advantages over the chemical precipitation method. Very much weaker solutions of cyanide can be used, down to as low as 0·05 per cent. cyanide, whilst for deposition by means of zinc a solution at least ten times as strong is necessary. The recovered gold is in a convenient form to handle, and the electrolytic installation necessary is comparatively inexpensive to instal. Sheet lead cathodes and iron anodes are employed. The anodes, 3 mm. thick, 2·1 metres long, and 0·9 metre wide, are enclosed in linen bags to prevent the Prussian blue formed anodically by the action of the cyanide electrolyte on the iron from contaminating the electrolyte.

The current density employed is usually from 0·005 to 0·01 ampere per 100 sq. cm. with an applied voltage of 3 to 4 volts, decomposition of the cyanide taking place with an E.M.F. above 5 volts. The electrolyte is slowly circulated through large wooden vats 30 feet long by 6 feet by 6 feet, which are divided into compartments so as to admit the electrolyte at the top and exit at the bottom of the cell.

Auric cyanide rapidly dissolves in excess of cyanide to form a practically colourless complex cyanide—

$$Au(CN)_3 + KCN \rightleftarrows KAu(CN)_4$$

The complex auric cyanide is dissociated in solution into potassion and the complex anion $Au(CN)'_4$, which is again dissociated according to the equation—

$$Au(CN)'_4 \rightleftarrows Au^{\cdot\cdot\cdot} + 4CN'$$

As in the case of complex copper cyanides, a very uniform, smooth and bright deposit of gold is obtained by this method. The gold, averaging from 2 to 12 per cent. in weight of the lead, is subsequently recovered by cupellation.

The disadvantages of the process are the difficulties inherent in the use of iron as anode material, the consumption of iron, and the contamination of the electrolyte by Prussian blue. According to Blount, Andrioli employs lead peroxide anodes and iron cathodes in a modification of this process; the lead peroxide anodes are said to be unaffected by the electrolyte. Tin foil and carbon have also been suggested. The gold deposited on the iron is removed by immersion in a bath of molten lead and subsequent cupellation. Keith suggests the co-deposition of mercury and gold to facilitate precipitation.

In the Haycroft process an electrolyzed brine leach is used, the chlorine being generated *in situ* by electrolysis between a mercury cathode situated at the base of the leaching chamber and carbon anodes suspended in the roof; the finely crushed ore in the brine is mechanically stirred and the leaching vat kept warm. The gold is removed from the ore partly by direct amalgamation and by electrolysis of the auri-chloride formed by the action of the liberated chlorine. The process does not seem to have passed the experimental stage. Clancy [29] has conducted some promising experiments on Haycroft's lines by using as electrolyte a mixture of KCN, KI and KCNS and calcium cyanamide, substituting the carbon anodes by the more refractory magnetite and using the iron leaching chamber as cathode. Efficient solution of the gold is claimed due to the formation of ICN at the anode. Cowper Coles has suggested the use of a slowly rotating aluminium cathode for the deposition of gold from a cyanide electrolyte. The gold deposit is said to be easily detachable from the electrode surface, and can be continuously removed in the form of a ribbon of thin gold sheet.

The Electrodeposition and Refining of Gold.[30]—In electroplating with gold, as in the case of the other metals discussed, copper and zinc, advantage is again taken of the uniformity and smoothness of deposits obtained by the use of a complex electrolyte. For electrolytes containing less than 0·1 per cent. gold the temperature of deposition should lie between 60° and 70° C. Reddish matte deposits are usually obtained. Cold electrolytes should contain more than 0·4 per cent. gold. The more important complex electrolytes used are the sulphocyanides, cyanide, ferrocyanide, and chloride; less important the phosphate, together with various electrolytes for producing coloured deposits.[31]

Cyanide Electrolytes.—The formation of a complex cyanide on the addition of auric cyanide to a solution containing excess of potassium cyanide takes place according to the following equations :—

$$\mathrm{Au(CN)_3+KCN \rightleftarrows KAu(CN)_4}$$

$$\mathrm{KAu(CN)_4 \rightleftarrows \dot{K}+Au(CN)'_4}$$

$$\uparrow\downarrow$$

$$\mathrm{Au^{\cdots}+4(CN)'}$$

When gold chloride is used as the source of the gold in the electrolyte, primary decomposition takes place according to the equation—

$$\mathrm{AuCl_3+3KCN=Au(CN)_3+3KCl}$$

Fulminating gold, $\mathrm{Au(NH_3)_2(OH)_3}$, is frequently formed as an intermediary by precipitation with ammonia to avoid the presence of chlorides in the electrolyte. Anodic solution proceeds smoothly in potassium cyanide electrolytes, but according to Jacobsen and Cohen,[32] in dilute sodium cyanide solutions the metal is liable to become passive owing to the formation of insoluble sodium aurous cyanide, $\mathrm{NaAu(CN)_2}$. The following bath suggested by Roseleur may be taken as typical of the cyanide electrolytes :—

Ten gms. of gold as chloride are dissolved in 250 c.c. of water and mixed with 20 gms. of potassium cyanide (98–99 per cent. pure) in 750 c.c. of water. Langbein recommends that this be boiled half an hour before use. Small current densities, with anodes of pure gold sheet, are usually employed from 0·12 to 0·41 ampere per 100 sq. cm., with a bath voltage of from 2·7 to 4 volts. The optimum temperature of deposition lies between 50° and 60° C. Dipping baths in which deposition is brought about by the insertion of sheet copper or zinc usually contain less potassium cyanide, so as to increase the concentration of gold ions in the solution.

Ferrocyanide Electrolytes.—The following reactions, according to Beutel,[33] take place in the formation of the potassium auric cyanide complex from a gold salt and potassium ferrocyanide:—

$$HCl.AuCl_3+K_4Fe(CN)_6+O_2 \rightarrow KAu(CN)_4+KCl+KCN +Fe_7(CN)_{18}+H_2O$$

His numerical relationships are, however, so complicated as to cast doubt upon this interpretation of the reactions taking place. The ferrocyanide baths formerly had the advantage over the cyanide electrolytes on account of their comparative cheapness and purity. With the modern methods of cyanide preparation these advantages no longer exist. They are not so poisonous as the cyanide baths, but on the other hand do not dissolve the gold anode so readily and the addition from time to time of auric chloride is necessary. Pfanhauser[34] recommends the use of 15·9 gms. of auric chloride, 90 gms. of ferrocyanide, with the addition of an equal amount of potassium carbonate per litre. The solution is boiled and the ferric hydroxide precipitate is filtered off. The temperatures and current densities are the same as those employed for cyanide electrolytes.

Chloride Electrolytes.—This electrolyte, originally suggested by Elsner[35] and studied by Bottger and Neumann,[36] was developed by Wohlwill,[37] and is the electrolyte employed at Hamburg for refining gold by the N. Deutsche Raffinerie.[38] Dr. Tuttle introduced the system with certain improvements into the Philadelphia Mint, where a large plant is now installed.

Crude gold containing both platinum and palladium is used as anode material, and large thin sheet gold cathodes are employed, the leads being of gold wire; soldered joints are avoided. The current density employed is, for the cathode 10 amperes per sq. dcm., and up to 30 amperes per sq. dcm. for the anode; the fall of potential over the bath is less than 1 volt. The electrolyte contains about 25 to 30 grammes of gold per litre as chloride, and about 3 per cent. of free hydrochloric acid, the temperature being maintained at 50° to 70°. The deposit of gold is uniformly pure and both adherent and crystalline, especially when a little gelatin is added to the bath. The solution contains the gold complex hydrogen aurichloride, which undergoes partial ionization according to the equation—

$$HAuCl_4 \rightleftharpoons H^{\cdot} + AuCl'_4 \rightleftharpoons H^{\cdot} + Au^{\cdot\cdot\cdot} + 4Cl'$$

It is important to have pure free hydrochloric acid in excess in the electrolyte to ensure the uniform solution of the gold anodes by the liberated chlorine. The primary formation of some aurous chloride, AuCl, at the anode probably takes place, with its subsequent decomposition into auric chloride and gold, which is either redeposited on the anode or falls as small crystals to the bottom of the cell—

$$3AuCl = AuCl_3 + 2Au$$

or is oxidized by the dissolved chlorine—

$$AuCl + Cl_2 = AuCl_3$$

thus serving as an anodic depolarizer. A very small amount diffuses into the bulk of the solution. At the cathode gold will be deposited in excess of that demanded by the deposition of trivalent gold due to the aurous ions present; consequently the weight of gold deposited is usually slightly more per ampere-hour than would be obtained from a solution containing only the trivalent gold ions. Platinum and palladium are recovered from the electrolyte when sufficiently concentrated by the usual precipitation methods. They are not cathodically deposited under the conditions of electrolysis. Osmium, iridium and silver chloride are recovered in the slimes. Over 70,000 ounces of gold per week are refined by this process in New York and Philadelphia alone.

The anodic solution potential of gold in a chloride solution is about $E_h = +1{\cdot}15$ volts, indicating that the bulk of the gold goes into solution in the trivalent state. On raising the anode potential the gold is apt to become passive, and chlorine will be liberated when the voltage has risen to +1·73 volts. Addition of chlorine ions lessens the tendency of the gold to become passive.

When relatively large amounts of silver are present in the anodes the use of asymmetric alternating currents is said to be attended with good results, preventing the silver chloride from adhering to the anode and thus raising the internal resistance of the bath. The use of bromide and iodide baths has been the subject matter of a few early patents.

Miscellaneous Electrolytes.—Withrow,[39] Perkin and Preeble[40] obtained good deposits with Wallace and Smith's[41] modification of Von Ruolz's patent, which utilizes the complex electrolyte formed on the addition of sodium sulphide to a gold salt, or by the solution of auric sulphide in excess of sodium sulphide—

$$Au_2S_3+3Na_2S \rightleftarrows 2Na_3AuS_3$$

The deposition of gold from this electrolyte, if similar to that of antimony from its complex sulphide (see p. 90), is not only due to the simple ionization of the salt according to the following scheme :—

$$Na_3AuS_3 \rightleftarrows 3\dot{Na}+AuS'''_3$$
$$AuS'''_3 \rightleftarrows Au^{\cdots}+3S''$$

but according to Ost and Klapproth,[42] the sodium sulphide plays an important rôle—

$$Na_2S \rightleftarrows 2\dot{Na}+S''$$

At the cathode the discharged sodion reacts both with the aurisulphide—

$$Na_3AuS_3+3Na=Au+3Na_2S$$

and assists in the intermediary formation of aurosulphide, according to the equation—

$$Na_3AuS_3+2Na=NaAuS+2Na_2S$$

whilst at the anode the sulphur converts the monosulphide into the yellow polysulphide—

$$Na_2S+S=Na_2S_2$$

The presence of excess of the polysulphide is objectionable if unattackable anodes are used as in electroanalysis, owing to the solvent action of this salt on the deposited gold according to the equation—

$$3Na_2S_2+2Au=2Na_3AuS_3$$

The addition of sodium sulphate or potassium cyanide to act as sulphur depolarizers have led to good results—

$$Na_2S_2+Na_2SO_3=Na_2S_2O_3+Na_2S$$
$$Na_2S_2+KCN=KCNS+Na_2S$$

At low current densities 0·1 to 0·3 ampere per sq. dcm. at 60° C., such electrolytes give excellent deposits.

Gold deposits can be tinted various colours by the admixture with other elements such as arsenic, lead, or more generally silver usually from cyanide baths.[43] Red gold can be obtained by the addition of a small amount of copper. One recommendation is to use both copper and nickel in the electrolyte.[44]

The Electrolytic Parting of Gold and Silver.—Not only does natural gold contain a certain amount of silver, from 5 to 50 per cent., but the silver slimes obtained in copper refining (see p. 40) also contain gold; according to Pring the average composition of silver slime is 15·3 per cent. copper, 45·5 per cent. silver, and 1·1 per cent. gold. The problem of parting gold from silver is therefore an important one in both these industries.

The silver slimes from the copper deposition tanks are washed, mixed with a small quantity of lead, and cupelled to doré bars, the arsenic and other impurities being volatilized during the process of cupellation.

The chemical process of parting by enrichment with silver until the alloy contains approximately only 20 per cent. gold with subsequent solution of the silver in nitric or sulphuric acid leaving the gold unattacked is being supplanted by the electrolytic method introduced by Moebius at the Deutsche Gold und Silber Scheide Anstalt at Frankfurt a. M., and is at work in mints at New York and Philadelphia.

The electrolysis is conducted in earthenware or wooden tanks, 2 ft. 6 in. deep and 3 ft. long, containing as electrolyte a mixture of nitric acid 0·1 to 1 per cent. and 2 to 4 per cent. silver nitrate[45] usually with a varying amount of copper nitrate when copper slimes are used. The doré metal anodes, ½ in. by 5 in. by 12 in. in size, enclosed in canvas or filter cloth bags, are separated about 6 in. from one another. Silver foil cathodes are inserted 3 in. distant from each anode. The silver is deposited at a high current density, usually from 2–3·5 amperes per 100 sq. cm. at 1·4–1·7 volts, to avoid interest charges on the silver. The loose feathery crystals which have to be mechanically detached from the electrodes are swept into canvas bags placed at the bottom of the vats. The mechanical scrapers usually employed, which also serve to agitate the electrolyte, are of wood and are of one of two forms. In the early form a wooden fork, the prongs of which scraped the two surfaces of the cathode plate, was suspended by a roller on a rail placed above each cathode and caused to run backwards and forwards, scraping off the crystals in its passage. A simplification introduced in America consists of a fork suspended some distance above the cathode and caused to oscillate backwards and forwards about its point of suspension (Fig. 6B).

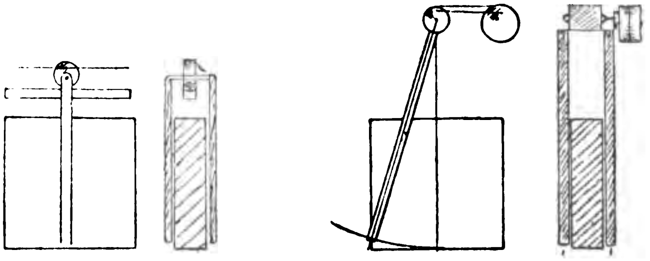


FIG. 6A. FIG. 6B.

Mechanical scrapers for the removal of deposits of silver crystals.

The silver crystals, which should contain no copper provided that the acidity of the bath is kept high and the current density employed not too great, are removed on the trays, allowed to drain, washed and melted into ingots.

The black pulverent anode slime, if washed and melted, consists of practically pure gold, but is liable to contain traces of lead or bismuth, or small pieces of the anode which have dropped off during the process of dissolution may contaminate the gold with silver and copper. These can be removed by treatment with acid. The slimes thus treated are cast into anodes and electrolytically refined for gold. Modifications of the plant have been suggested with a view to the elimination of the wooden scrapers, such as the employment of a moving silver band as cathode. It is placed at the bottom of the vat with a number of horizontal anodes separated from it by canvas diaphragms placed above. The process is in use at Monterey in Mexico. The crystals deposited on the moving cathode are removed by scraping and elevated out of the bath by another travelling band.

At Balbach, U.S.A., Thum's modification of the Moebius plant is worked with success. Horizontal anodes separated by cloth diaphragms are employed as in the Mexican works, but the travelling silver band cathode is replaced by graphite block cathodes on which the silver crystals are deposited. A slightly lower current density is employed, viz. 1·8–2 amperes per 100 sq. cms. at a higher voltage, 3·5 volts, owing to greater distance between the electrodes and the interposition of the slimes. Mechanical agitation is dispensed with, but the crystals are pressed down from time to time to the bottom of the vat.

The conditions necessary for the separation of silver without any copper in the electrolytic parting of gold and silver are in practice very simple, viz. a high acidity and a low current density. As, however, the metals locked up in the vats are a great deal more valuable than copper, low current densities are even more economically unsound than in copper deposition, and in practice must be maintained as high as possible. From 2 to 3 amperes per 100 sq. cms. with an E.M.F. of 1·2 to 2 volts per cell are usually employed, although in certain cases up to 6 amperes per 100 sq. cms. have been used, the current density being decreased as the concentration of the copper salts increases. In a solution containing normal cupric ion and normal silver ion the discharge potentials of the copper and silver are —0·324 and —0·771 volt respectively, there being a difference between the two discharge potentials of nearly 0·5 volt. The decomposition potential voltage of a normal silver nitrate solution is about 0·70 volt, and since in practice the electrolytes used are considerably weaker than normal, being approximately between 0·1 and 1 normal in respect to the silver, this minimum decomposition voltage is therefore slightly higher than 0·70 volt, and can be raised nearly 0·5 volt without any copper commencing to be deposited. The usual operating voltage lies between 1·28 and 1·35 volts. In the processes carried out in the mints where the anodes contain over 30 per cent. gold, no diaphragms are used, but the vats are run at a low current density of 0·8 ampere per sq. dcm., attention is paid to obtaining an adherent deposition, while the gold remains behind as an anode skeleton. The addition of free nitric acid is necessary, up to 1 per cent. acid, to neutralize any ammonia which may be formed by the possible reduction of the nitrate ion taking place at the cathode. The presence of even small quantities of basic salts results in a formation of a spongy deposit. Occasionally the silver crystals which are deposited are not white, but dulled due to the formation of an unstable oxide; the addition of a small quantity of alcohol corrects this tendency. Large crystals can be reduced in size by the addition of 1 part in 10,000 of gelatine, but the addition of gelatine must be made every day, as it is partly destroyed by the nitric acid and partly removed in the deposited silver. When the electrolyte has become rich in copper salts (0·4 per cent.), the silver in the spent electrolyte can be recovered by the addition of copper or precipitation as chloride. Subsequent removal of the copper by electrolysis or chemical deposition with iron is usually employed.

SILVER.

The electrolytic recovery of silver from its ores by the application of the methods of electrochemical deposition from one of the usual leaching agents employed in the wet processes of silver extraction does not seem to have received any attention, chemical precipitation by means of scrap iron or copper being usually employed. Present day economic conditions have shown that the electrolytic winning of copper may be remunerative in certain localities, and the electrolytic recovery of silver would probably be even more favourable. As in the case of gold a cyanide leach would probably offer several advantages.

The electrolytic refining of silver is now practised extensively, utilizing crude silver containing gold, copper and lead together with many minor impurities. The Pennsylvanian Lead Co. at Pittsburg use crude silver anodes containing 2 per cent. lead, bismuth and copper, whilst the New York and Philadelphia refineries use 30 per cent. gold, 60 per cent. silver, and 10 per cent. base metal as anode material. Electrolytic refining could possibly be substituted for cupellation of the zinc-lead-copper complexes obtained in the various processes for removing silver from lead. The parting of gold and silver as well as the practical conditions to be observed in the refining of silver from nitrate electrolytes have already been discussed.

Electroplating with Silver.—The nitrate electrolyte is unsuitable for electroplating; the deposit is macrocrystalline and spongy, probably owing to the formation of a suboxide[46] or due to the absorption of oxygen.[47] The deposit can be improved by rapid agitation or rotation of the cathode as shown by Sand[48] and Snowden,[49] by the addition of alcohol as suggested by Küster,[50] or by the addition of small quantities of colloids such as gelatine. These improved silver deposits, although sufficiently good for silver refining purposes or even for electroanalysis, are not suitable for plating.

Cyanide Electrolytes.—The cyanide complex silver electrolyte is probably, in common with those of copper and gold, the most suitable electrolyte for silver deposition. Dissociation in the electrolyte proceeds according to the following equations:—

$$AgNO_3+KCN=AgCN+KNO_3$$

The precipitate of silver cyanide is soluble in excess of cyanide to form the soluble potassium silver cyanide which is dissociated—

$$\begin{gathered}Ag(CN)+KCN\leftarrow KAg(CN)_2\\ KAg(CN)_2\rightleftarrows\dot{K}+Ag(CN)'_2\\ Ag(CN)'_2\rightleftarrows\dot{Ag}+2(CN)'\end{gathered}$$

The presence of the salt formed due to the decomposition of the silver salt by the potassium cyanide has a considerable influence on the nature of the deposit, the nitrate, chloride, oxide, used originally by A. & H. Elkington in Sheffield in 1840, and carbonate of silver have all been advocated, whilst other investigators insist on the primary separation of the insoluble silver cyanide from the soluble salt making up the electrolyte. Langbein advocates the use of the chloride, but states that beyond certain limits the presence of chlorides is apt to give the deposit a coarse structure.[51] Pfaunhauser uses 10 gms. of silver as chloride and 20 gms. of potassium cyanide per litre. With electrodes 10 cms. apart and a current density of 0·3 ampere per 100 sq. cms. the potential drop across the bath being about 1·25, a good deposit is obtained. For heavier coats he suggests 25 gms. of silver as chloride, with 40 gms. potassium cyanide per litre and the same current density.

"Striking" baths for giving a preliminary thin coat for certain work such as steel are generally very weak in silver. A good electrolyte contains about 1·5 gms. of silver with 70 gms. of potassium cyanide per litre. A high current density should be employed to ensure a brisk evolution of cathode hydrogen. Foerster and Namias[52] advocated double cyanide baths without the presence of any neutral salt. The former suggests 25 gms. of silver cyanide and 25 gms. pure potassium cyanide per litre, using a current density of 0·3 ampere per 100 sq. cms., with a P.D. of 1 volt.

The use of addition agents to cyanide electrolytes for obtaining bright instead of matte deposits is very usual, especially for plating articles which cannot easily be burnished. Carbon disulphide has been used as an addition agent since 1847. The quantity added should not exceed 2·5 parts per 10,000; agitation of the bath should be avoided, and the current density should be a little higher than normal. Other but less effective addition agents have been suggested from time to time; amongst the more important may be mentioned iodine or iodine and guttapercha in chloroform, or a mixture of sulphur and collodion. The use of a suspension of silver sulphide has also been suggested. The use of these addition agents as brighteners appears to be a particular case of the action of protective colloids such as glue, linseed oil, mucilage or gelatine.

Miscellaneous Electrolytes.—Some of the earlier experimenters advocate the use of ferrocyanide electrolytes. Elsner [53] dissolved 7 gms. of silver in a solution of 8·4 gms. of potassium ferrocyanide, 56 gms. of ·880 ammonia, and 1 litre of water. These solutions have not been extensively used, as they do not dissolve the silver anodes in a regular manner.

Krutwig [54] claimed that silver could be deposited from a silver hydroxide ammonia electrolyte provided that rapid agitation of the electrolyte was ensured. The presence of a reducing agent such as sulphurous acid or sodium thiosulphate is necessary. Various organic acids such as the lactates, acetates, citrates have been the subject of patents, but are not so efficient as the cyanide electrolytes already discussed.

LEAD.

The Electrolytic Recovery and Refining of Lead.—The common lead ores consist of lead zinc sulphide complexes containing varying amounts of gold and silver. In the usual thermal treatment the sulphide ores are first roasted. During the process of roasting two series of reactions proceed simultaneously according to the equations—

$$\left.\begin{array}{l} 2PbS+3O_2=2PbO+2SO_2 \\ PbS+2O_2 \;=PbSO_4 \end{array}\right\}\text{Roasting processes.}$$

$$\left.\begin{array}{l} PbS+PbSO_4 \;=2Pb+2SO_2 \\ PbS+2PbO=3Pb+SO_2 \end{array}\right\}\text{Reduction processes.}$$

If the general procedure of adding lime be followed a further side reaction takes place—

$$PbSO_4+CaO \rightleftarrows CaSO_4+PbO$$

This roasted ore, containing varying amounts of PbO, $PbSO_4$, and lead, is then reduced in a blast furnace by means of coke. The molten lead separates to the bottom, leaving on top a mixture of lead, iron, and copper sulphide. The crude lead so separated has approximately the following composition :—

Pb	98·3
Cu	0·186
Sb	0·720
As	0·006
Bi	0·005
Ag	0·141
Fe	0·001
Zn	0·003
Ni	0·0023
Co	0·0002
Cd	trace

Frequently also a small quantity of gold. It is then submitted to refining processes which will be described later. The purely thermal process of roasting and reduction to obtain crude lead is an economical one, since the heats of formation of the oxide and sulphide are low, permitting of easy reduction, and the low melting-point of the metal ensures an easy removal from the furnace. Any electrolytic treatment of the ore that could compete with this process would be one in which the direct production of the pure metal and the other by-product sulphur, either as such or as hydrogen sulphide or sulphur dioxide, was ensured with the minimum expenditure of electrical energy; at the same time permitting of the extraction of the valuable impurities in the ore by some simple process.

It has generally been assumed that the low cost of purely thermal processes would prevent the development of any electrolytic process on a technical scale. The following calculation will show, however, that if some such process could be developed, the economic aspect of the question is entirely in its favour:—

One ampere second will deposit 1·072 mgms. of lead, hence a metric ton (1000 kgms.) will require 277 kiloampere hours. Lead sulphide can be decomposed with an applied E.M.F. of about 1·1 volts, or 1 metric ton of lead could be deposited by 300 kilowatt hours. With a kilowatt hour costing as much as 0·5*d.* this only entails an expenditure of 12*s.* 6*d.*, whilst the estimated cost of thermally refining crude lead alone exceeds 25*s.*

Betts and Valentine[55] have made several experiments on the electrolysis of lead sulphide dissolved in molten lead chloride. They state that a good deposition of molten lead can be obtained below a red heat with an applied E.M.F. of 1·0 to 1·25 volts. The presence of impurities in the galena, however, has prevented this process from being developed on an industrial scale. Anderson[56] attempted unsuccessfully to electrolytically reduce galena in a fluosilicate solution. In the Salom process worked at Niagara, lead sulphide finely ground was admitted into a lead chamber serving as cathode and container, with a 10 per cent. sulphuric acid electrolyte. At a voltage of 2·5 to 2·9 volts per cell a current efficiency of 70 per cent. was attained, the sulphide being cathodically reduced to spongy lead and H_2S.

Scarcely any attempts have been made to work up the roasted ore electrolytically. The problem is analogous to the recovery of lead from the lead sulphate scrapings obtained in the lead chambers of sulphuric acid works. Lead sulphate is soluble in sodium acetate and caustic soda; from both these electrolytes good deposits of lead may be obtained. In the case of the roasted ore which contains, in addition to the lead sulphate, both metallic lead and lead oxide, the possibility of casting it directly into anodes presents itself. Burleigh[57] suggested the solution of the roasted ore in hot concentrated soda, where deposition of lead could be obtained with an impressed E.M.F. of 1·7 volts.

The Refining of Lead.—Although not much progress can be recorded in the electrolytic process for the recovery of lead several schemes have been suggested for refining the crude lead electrolytically, and of recent years various improvements have so modified the process that it is now much more economical than either the Pattinson or Parkes refining processes. In the Pattinson process the crude lead is subjected to an oxidizing melt. The bulk of the zinc, iron, and nickel is removed by steam injection, whilst the tin, arsenic, and antimony are removed by introducing air, forming stannate, arsenate, and antimonate of lead, which come to the surface and are removed. On fractional crystallization the first fraction consists of a copper-lead alloy which contains the rest of the nickel, cobalt, sulphur, and arsenic; removal of the bismuth is never complete. In the Parkes desilverizing process zinc is added to the partially purified molten lead, when an alloy of gold and silver is formed which solidifies on the surface of the molten lead. The solidified alloy is removed and the zinc removed by distillation. During the process of distillation a small quantity of silver is also lost up to 1½ per cent. For leads very rich in silver (over 12 oz. per ton) the whole of the lead can be removed as litharge by an air blast, leaving the silver and gold behind on the cupel, the oxide lead being then again reduced to metal.

The earliest electrolytic process for refining lead was that of Keith. Crude lead anodes in muslin bags to retain the slimes were used in an electrolyte of lead acetate or lead sulphate dissolved in sodium acetate. Lead was deposited on the thin sheet lead cathodes as small crystals, which fell to the bottom of the cell and were removed and fused together. The electrolyte contained 20 gms. of lead sulphate and 150 gms. of sodium acetate per litre. The current density employed varied from 0·2 to 0·35 ampere per 100 sq. cms. at 0·4 to 0·5 volt. Tommasi employed a rotating cathode in the form of an aluminium bronze disc of 3 metres diameter mounted on a horizontal axis performing 2 rotations per minute. A current density of 7·2 amperes per 100 sq. cms. could be employed. By means of scrapers on each side of the disc the lead crystals could be removed on to a sieve conveyor to be drained, washed and fused with a little charcoal.

The Betts[58] process is in use at Trail, B.C., near Chicago, and at Newcastle-on-Tyne, England, and may be said to be the most successful of electrolytic lead-refining processes. Crude lead is melted and cast into anodes about 75 by 75 by 2 cms. extending to 3·8 cms. at the top in size. Each anode is cast with lugs and weighs about 170 kilos, being separated from the next anode by a distance of 11·3 cms. The cathodes are refined sheet lead not over 1·2 cms. thick when finished. The electrolytic tanks are 6 feet long, 2 feet 6 inches wide, and 3 feet 6 inches deep, made of wood lined with bitumen, and hold 22 anodes and 21 cathodes each. The current density employed varies from 0·9 to 2·2 amperes per 100 sq. cms., and the applied E.M.F. from 0·15 to 0·42 volt, the E.M.F. gradually rising as the slime adheres to the anodes. Even when the anodes are nearly completely dissolved they still retain their original form. The electrolyte consists essentially of a solution of lead silicofluoride in free fluosilicic acid, first suggested by Leucks.[59] Thirty-five per cent. hydrofluoric acid is repeatedly filtered through quartz, and lead carbonate is added to the resulting fluosilicic acid, until the solution contains 60–90 gms. of lead per 100 gms. of free fluosilicic acid. The optimum temperature lies between 30° C. and 35° C.

Pring[60] gives the following suitable electrolyte :—

H_2SiF_6	9·5–10·5 per cent.
Pb as $PbSiF_6$	4·5–5·2 per cent.
Sp. gr.	1·13–1·16

It has been found necessary to add a small quantity of colloid such as glue or gelatine not exceeding 0·1 per cent.

and generally about 1/5000. Owing to its destruction at the anode, where it prevents the formation of lead peroxide, frequent small additions are necessary. At Trail, B.C., 0·007 per cent. of glue is added every other day. The following analyses are typical of the deposited lead and the slimes :—

Impurities in the lead.			Slime.		
Cu	0·0010	per cent.	Pb	10·3	per cent.
Bi	0·0022	„	Ag	4·7	„
As	0·0025	„	Sb	25·32	„
Sb	0·0017	„	As	44·58	„
			Bi	0·52	„
			Cu	9·3	„

Betts has suggested the use of other addition agents in addition to glue and gelatine, such as pyrogallol, phenol, resorcin, and saligenin, including anodic depolarizers like sulphurous acid, hydroquinone, and o.amidophenol. The current yield is said to be from 85 to 90 per cent. Senn[61] and Kern[62] confirmed the utility of Betts' electrolyte. Fischer, Thiele and Maxted[63] also obtained good deposits with fluosilicates, fluoborates, fluozincates, and fluostannates.

Various other electrolytes, in addition to fluosilicic acid salts, have been suggested and are the subject matter of numerous patents. Siemens and Halske[64] have patented the use of lead perchlorate containing free perchloric acid and an organic colloid as an electrolyte. It is said that the Hagener accumulator works are using this electrolyte on a large scale. Peptone appears to be the best addition agent for perchlorate baths, although mucilage, albumen, salep, and other vegetable mucilages have been patented by the same firm.

A suitable bath was found in an electrolyte containing

Pb as perchlorate, 5 per cent.
$HClO_4$, 2-5 per cent.
Peptone, 0·05 per cent.

A current density of 2–3 amperes per sq. dcm. at a voltage of 0·21 with electrodes 2·5 cms. apart, gave solid smooth deposits with a current efficiency of over 99 per cent.

Mathers and Overman [65] found the most suitable addition agents in order of merit to be—

Clove oil	100 c.c. per ton of lead deposited.
Peptone	350 gms. „ „ „
Phloridizin.	

Snowden [66] modified the Tommasi process by using a cathode rotating at high speed and 0·1 per cent. of gelatine in the acetate electrolyte. The use of nitrate solutions as well as complex electrolytes, such as lactates and oxalates, have been investigated, but the deposits obtained from the solutions are not as good as those from the electrolytes already enumerated.

The electroplating of metals with lead as protection against acid corrosion with the above electrolytes has not come up to expectation.

Difficulties have been encountered in the satisfactory treatment of the slimes recovered in the electrolytic lead-refining plants. The slimes contain lead, arsenic, and antimony, with smaller traces of copper, iron, silver, and more rarely bismuth, gold, and tellurium. One of the most satisfactory methods of dealing with this complex is the one adopted at Trail. After washing with water and weak alkali to remove the last traces of acid the slimes are boiled in a 6 per cent. sodium sulphide solution, containing about 1 per cent. Na_2S_2. Antimony is thus removed and recovered by electrodeposition (see p. 90). The slimes are then leached with hot sulphuric acid in the presence of air. From the solution the silver and copper are removed and gold recovered from the residue. Other methods, such as extraction of the antimony with hydrofluoric acid, to which is then added sodium potassium fluoride and the antimony recovered by electrodeposition, whilst the residues are subjected to chlorination and fractional electrolytic precipitation, amalgamation processes or casting the slime into anodes with subsequent electrolytic treatment, have all been suggested, but details of technical working are lacking for the majority of these suggestions.

ANTIMONY.

The electrolytic deposition of antimony has been developed on a technical scale by Siemens and Halske. As electrolyte a solution of antimony sulphide in sodium sulphide is used, the antimony sulphide ore being leached with the spent electrolyte. In the original process a divided cell was used, the antimony being deposited from the circulating catholyte on sheet iron cathodes, whilst in the anode compartment where carbon anodes are placed, chlorine is liberated from a salt solution. At Trail, where lead slimes are used as a source of antimony, the divided cell is dispensed with, and the sodium sulphide is allowed to be partially oxidized at lead anodes to sodium sulphite and sulphate. With a current density of 0·7 amp. per sq. dcm., with an applied E.M.F. of about 1 volt and an electrolyte temperature of 60° C., antimony practically pure is deposited as a dull warty sheet about 3 mm. thick. The deposited metal is removed by melting under a flux of soda and potassium sulphide, which effectually removes the last traces of sulphur, and cast into ingots showing the characteristic stellate crystalline structure.

A 6 per cent. solution of sodium sulphide is used as solvent and electrolyte; antimony pentasulphide dissolves in this solution as follows :—

$$Sb_2S_5+3Na_2S=2Na_3SbS_4$$

which partially dissociates into the following :—

$$Na_3SbS_4 \rightleftarrows 3\dot{Na}+SbS_4{}'''$$

Since the complex SbS'''_4 is not readily dissociated again—

$$SbS'''_4 \rightleftarrows Sb^{\cdots}+2S'+2S''$$

the equilibrium of $Sb^{\cdots}$ ions in a 6 per cent. solution of antimony sodium sulphide being only $10^{-60}{}_n$ ($E_hSb/N.Sb^{\cdots} = -0{\cdot}463$, whilst $E_hSb/\frac{N}{10}Sb^{\cdots}$ in $Na_2S=+0{\cdot}709$ volt). Ost and Klapproth[67] assumed that the deposition of antimony was caused by the secondary reaction caused by the discharge of sodions at the cathode as follows :—

$$5Na+Na_2SbS_4=Sb+4Na_2S$$

Whether the mechanism is a direct electrodeposition of antimony or is caused by a secondary decomposition, there is always an anodic liberation of free sulphur. Free sulphur reacts with sodium sulphide to form the polysulphide—

$$Na_2S+S=Na_2S_2$$

which on diffusion to the cathode will dissolve antimony to form a thioantimonate—

$$2Sb+3Na_2S_2=2Na_2SbS_3$$

Consequently only a low current efficiency can be claimed in a single cell process such as is used at Trail, unless a sulphur depolarizer is added to the electrolyte, the average efficiency lying between 45 and 50 per cent. Among the more important sulphur depolarizers which have not yet received technical application may be mentioned sodium sulphite and potassium cyanide—

$$Na_2S_2+Na_2SO_3=Na_2S_2O_3+Na_2S$$
$$Na_2S_2+KCN=KCNS+Na_2S$$

Experiments have also been conducted with other electrolytes in addition to the alkaline sulphides. At Newcastle-on-Tyne antimony is deposited from a solution of the fluoride in an electrolyte of hydrofluoric acid containing potassium and sodium fluoride. Betts[68] has suggested the use of acid solutions containing iron salts in a divided cell, the ferric salts generated anodically being used to dissolve more antimony from the slimes. Successful electrolytes were found in the mixtures of antimony trichloride and trifluoride with the addition of ferrous sulphate or chloride.

BISMUTH.

The technical electrodeposition of bismuth has not been successfully developed on a large scale. Although the electrolytic potential of bismuth in a solution containing its ions lies considerably below the point where hydrogen evolution should commence $E_h=-0{\cdot}393$ volts, yet, owing to the tendency for this element to form complex salts in solution hydrogen, evolution is unavoidable. Under these conditions bismuth is deposited, either in a spongy condition or as closely adherent crystals, with a very low current efficiency. Foerster and Schwabe[69] claim to have obtained good deposits from a fluosilicate solution, whilst Sand[70] obtained deposits suitable for electroanalytical work from nitrate solutions.

Excellent deposits may be obtained from sodium tartarate and oxalate solutions provided that the cathode potential is carefully adjusted continuously during the deposition.

The regulation of the cathode potential could possibly be eliminated if a divided cell were used, in which a constant anodic depolarisation under a constant current density and a carefully regulated terminal voltage could be maintained.

TIN.

There has been no electrolytic process devised for the winning and refining of tin. The usual metallurgical methods are sufficiently simple and economical (m.p. Sn =233° C.), and the impurities in crude tin, chiefly lead, antimony, and iron, with but small traces of silver and gold, are not sufficiently valuable, totalling only 1 to 1·5 per cent., to warrant an electrolytic refining process. Various extraction processes have been the subject of patent literature, but have not become technically successful, amongst which may be mentioned—

Fusion Processes.—(A) Fusion of the ore with caustic soda and subsequent leaching with water and electrodeposition, according to Goldschmidt's process.

(B) Fusion with soda and sulphur and subsequent leaching with water and electrodeposition from the thiostannate solution according to Claus's process.

Leaching Processes.—(A) Alkaline leaching with caustic soda or caustic soda containing sodium sulphide.

(B) Acid leaching with sulphuric, hydrochloric of acid ferric chloride solutions.

The recovery of tin from scrap iron plate has, however, become an important electrochemical industry, and has led to an investigation into the most suitable conditions for the deposition of tin. Although the Goldschmidt chlorine stripping process is extensively employed and with the growing supply of chlorine gas at low prices is likely to extend, yet the electrolytic processes have been developed and are as yet holding their own. Before the war over 30,000 tons of tin scrap per annum found their way to Germany for detinning. Tin plate averages some 2·5 to 5 per cent. tin by weight, and the residual iron is in great demand for electric furnace steel work. The more important electrolytic detinning processes may be classified as follows:—

A. Alkaline Electrolytes.

(1) *Beatson's Process*[71] developed by Goldschmidt.[72] The scrap tin plate is compressed, perforated, and washed with caustic soda to remove fats and paint. About 15 kilos of the clean tin scrap is loosely packed in an iron cage and suspended in an iron tank which serves as a cathode. The electrolyte is an 8 per cent. caustic soda solution, and must be regenerated from time to time, since it is continually being used up by absorption of carbon dioxide; when the concentration of alkali becomes too low stannic hydroxide separates from the electrolyte.

The temperature of the electrolyte is maintained at 70° C. by steam heat, and the current density of 0·80 to 1 amp. per 100 sq. cms., with an E.M.F. of 1·7 volts (which rises to 2·5 volts when detinning is complete). The tin is deposited from the solution in a spongy form containing a little copper, iron, and lead with an 80 per cent. current efficiency (assuming solution and deposition of tetravalent tin). The sponge is compressed and melted with coke. Foerster and Dolch investigated the mechanism by which the tin is dissolved at the anode and deposited on the cathode.[73]

Dissolution and precipitation of the tin in the tetravalent state have been shown to take place—

$$Sn \rightarrow Sn^{\cdot\cdot\cdot\cdot}$$

with a current efficiency of 80 per cent., but it appears more probable that dissolution takes place as follows:—

$$Sn \rightarrow Sn^{\cdot\cdot}$$

the divalent alkaline stannite being anodically oxidized by the oxygen liberated. Tin becomes readily passive in alkaline solution owing to the formation of a film of colloidal stannic hydroxide; when this occurs the anodic potential is raised sufficiently to cause the evolution of oxygen. Cathodic reduction of $Sn^{\cdot\cdot\cdot\cdot}$ to $Sn^{\cdot\cdot}$ before deposition does not appear to take place.

Gelstharpe[74] favours agitation of the electrolyte, which reduces the applied E.M.F. for stripping and deposition by about 0·5 volt. Borchers[75] and Keith[76] advocated the addition of sodium chloride to the alkaline electrolyte. If more than 3 per cent. of sodium chloride is added iron is also dissolved. Sodium nitrate as well as sodium cyanide have been advocated as addition agents with unsatisfactory results.

(2) *Borchers' Process.*—Borchers proposed an electrolyte containing 15 per cent. sodium chloride and 3 per cent. of sodium stannate as electrolyte. With a temperature of 50° C. and a P.D. of 2–3 volts per cell, tin could be effectually stripped and deposited with a current density of 0·5 to 1·5 amps. per 100 sq. cms. Luckow advocated a fluoride bath for the same purpose.

(3) *Claus's Process.*—As electrolyte, a solution of sodium thiostannate was used,[77] containing 4–5 per cent. tin and 10 per cent. of free caustic soda. Electrolysis takes place in a warm electrolyte at 80° C. with sheet iron cathodes and a current density of 3–4 amperes per 100 sq. cms. All impurities except arsenic and antimony are removed as slimes. Steiner[78] advocated the addition of 1 per cent. of flowers of sulphur to the electrolyte.

B. Acid Electrolytes.

(1) *The Neil and Brown Process.*[79]—The scrap tin plate is stripped in boiling ferric chloride solution according to the equation—

$$2FeCl_3+Sn\rightarrow 2FeCl_2+SnCl_2$$

The disadvantage of this process is the simultaneous solution of iron during the period of immersion. The electrolyte is circulated through divided cells of concrete first through the cathode, then back through the anode compartments. The cathodes are sheet tin, and separated from the graphite anodes by earthenware diaphragms. At the cathodes tin is deposited—

$$\mathrm{Sn}^{\cdot\cdot}\rightarrow\mathrm{Sn}+2\oplus$$

whilst at the anodes the ferric chloride is regenerated—

$$2\mathrm{FeCl}_2+2\mathrm{Cl}'=2\mathrm{FeCl}_3+2\ominus$$

Provided that the tin plate could be stripped without simultaneous solution of iron this process would be more economical than the Goldschmidt one. Hemingmay[80] uses ferric sulphate as a leach. Divided cells are not used, but the ferrous sulphate is reoxidized by sodium nitrate.

(2) *The Bergsoe Process.*—Cold tin tetrachloride is used as stripping solution, the tin going into solution as follows :—

$$\mathrm{SnCl}_4+\mathrm{Sn}\rightarrow 2\mathrm{SnCl}_2$$

Tin cathodes and graphite anodes are used. The process is open to the same objection as the Brown, namely the simultaneous solution of iron with the tin. Rienders[81] conducted experiments on stannous chloride and stannic acid solutions as electrolyte with the addition of ammonium chloride. Solution of the tin proceeds both chemically and electrochemically in the stripping cell, and the excess of tin in solution is subsequently removed in separate cells, utilizing graphite anodes. A current density of 1 to 2 amperes per 100 sq. cms. is employed.

Gelstharpe[82] carried out successful experiments at Manchester with a 1·25 per cent. solution of hydrochloric acid containing a trace of sulphuric acid as electrolyte ; with a current density of 1·7 amperes per 100 sq. cms. at 1·5 volts practically pure tin sponge could be obtained.

Sulphuric Acid stripping and depositing electrolytes have been suggested by Smith and Englehardt,[83] the latter claiming a current efficiency of over 60 per cent. Nauhardt suggested the addition of a small quantity of ammonium sulphate. A good deposit was obtained with a current density of 0·2 to 0·3 ampere per sq. dcm. Quintaine[84] deposited tin from a sulphate solution on lead cathodes. Nodin [85] used sulphuric acid as a stripping agent, followed by electrodeposition in separate cells on the basis of the Neil and Brown process.

C. Miscellaneous Electrolytes.

Matuschek [86] has suggested the use of ammonium oxalate dissolved in a saturated solution of tin ammonium chloride as a suitable stripping and depositing electrolyte. Good deposits could be obtained at current densities as high as 3 amperes per 100 sq. cms., provided some colloidal addition agent were employed. Tannin, gum, and a small quantity of NaH_2PO_4 were stated to be most suitable. Hollis [87] suggested the use of tin fluosilicate as a suitable electrolyte. Mennicke [88] observed that the best conditions for deposition were obtained with an electrolyte containing 10 per cent. tin and 10 per cent. free hydrochloric acid. Electrolysis was conducted with a current density of 1 ampere per 100 sq. cms. at 20° C.

The alkaline electrolytes suffer in practice from their instability in presence of atmospheric carbon dioxide, and the fact that the iron tin alloy formed at the junction of the two metals is not dissolved. The whole of the tin is removed by acid electrolytes, but the simultaneous solution of the iron which has already been referred to renders these stripping agents even more unsuitable than the alkaline ones.

Tin Plating.—There are many difficulties associated with the electrodeposition of tin as a white dense adherent deposit. Not only do the anodes dissolve irregularly in excess of the amount deposited on the cathode, but the deposited metal is generally dull, powdery, and loosely adherent. Special precautions as regards cleanliness of the surface which is to receive the deposit have to be taken.

Iron and steel are generally given a thin copper deposit before the tin coat to ensure adherence of the tin, due to the formation of alloys, Cu_3Sn, Cu_2Sn. Very low current densities must be employed, and as electrolytes those which form complex ions are found most suitable. For good deposition high temperatures and efficient circulation of the electrolyte are essential. Thick, dense deposits can only be obtained by rotating the cathode at high speed or by removing the electrode from time to time and scraping the deposit with a fine wire brush.

Alkaline Electrolytes.—Twenty-five grammes of stannous chloride dissolved in a litre of water containing 60 gms. of caustic soda or 20 gms. of caustic potash forms a suitable electrolyte. With a current density of 0·1 ampere per 100 sq. cm. good deposits may be obtained. Steel and Elsner[89] recommended the addition of potassium cyanide to the electrolyte. In the *Brass World*[90] the following electrolytes for giving good deposits on brass and iron are stated :—

(1) *On Brass*—

	Gms. per litre.
KOH	7·5
$SnCl_2$	7·5
KCN	35·0

(2) *On Brass or Steel*—

KOH	15
$SnCl_2$	15
KCN	35

It is recommended to use the solutions warm and electrolyze with a bath voltage of 2·5 to 3 volts. A large anode surface is desirable.

Acid Electrolytes.—The use of acid oxalates and pyrophosphates in acid solution form the basis of a great number of electrolytes for tin deposition. Roseleur's electrolyte is the most generally used, and gives satisfactory deposits. Pure tin anodes must be employed, and the electrolyte containing 12·5 gms. of sodium pyrophosphate and 1·5 gms. of stannous chloride per litre must be kept hot. Field[91] mentions an oxalate bath of the following composition :—

	Grammes per litre.
Stannous chloride	25–30
Acid ammonium oxalate	55–65
Acetic acid	3–4

The bath is conveniently worked at 65° C. with a current density of 1 ampere per 100 sq. cm. Other solutions containing tartaric and lactic acids have also been suggested. Kern[92] gives a résumé of the work published on the deposition of tin and has further investigated the effect of addition agents in the nature of the deposit. Tannin in the proportion of 1 gramme to 1·5 litres of solution was found to be the most beneficial in stannous chloride and fluoride solutions.

NICKEL.

The electrolytic recovery of nickel from its ores, chiefly sulphide and arsenide, is associated with difficulties, inasmuch as the nickel ore always contains relatively large quantities of copper and iron. Attempts to use nickel matte anodes in a nickel sulphate or chloride electrolyte have not proved technically successful, although Günther[93] obtained good and uniform solution of such electrodes in a sulphate solution. The sulphur is liberated in a free state at the anode. W. Trumm[94] developed a process for the Orford Copper Co. using nickel sulphide electrolytes in a nickel chloride solution. It is said that the process proved satisfactory on a small scale.

As in the case of copper either desulphurization of the matte, or extraction processes are necessary to avoid unduly fouling the electrolyte. The Canadian Copper Co. have experimented successfully on a desulphurized nickel matte containing both copper and iron, casting the same into anodes. As electrolyte, a chloride solution was used, obtained by chlorine treatment of desulphurized matte in a brine solution. Electrolysis was conducted in a series of concrete vats; in the first series, with an applied E.M.F. of 0·35 volt, copper was deposited on electrolytic copper sheet cathodes. When the ratio nickel to copper in the electrolyte exceeded 80 : 1 the rest of the copper was precipitated by sodium sulphide, the iron removed as hydroxide, and the bulk of the salt removed by concentration. The nickel was finally removed by deposition on nickel sheet cathodes, using graphite anodes enclosed in earthenware diaphragms to remove the chlorine. With an applied E.M.F. of 3·5 to 3·6 volts, nickel over 99·85 per cent. in purity could be deposited with a current efficiency of 93 per cent.

EXTRACTION PROCESSES.—Hoepfner (see p. 35) modified his electrolytic process for copper ores which has already been discussed, to nickel. After roasting the ore to render the iron insoluble, extraction of the copper and nickel sulphides was accomplished by means of a solution of cupric chloride containing calcium chloride according to the equation—

$$\mathrm{NiS} + 2\mathrm{CuCl_2} \rightarrow \mathrm{Cu_2Cl_2} + \mathrm{NiCl_2} + \mathrm{S}$$

The silver and iron having been removed chemically and the copper electrically, the electrolyte containing but little copper and all the nickel was passed on to cells of similar construction as used for removing the copper, but a nickel sheet cathode was substituted for a copper one. The graphite anode was depolarized by the returning cuprous and nickelous chloride solutions.

The separation of copper and nickel can be made nearly complete by adjustment of the cathode potential, as is indicated by the following figures for the cathodic potential equilibrium values between the metals and their solutions :—

$\mathrm{Ni}/n\ \mathrm{Ni}^{\cdot\cdot}$ salt $E_h = +0{\cdot}228$ volt
$\mathrm{Cu}/n\ \mathrm{Cu}^{\cdot\cdot}$ salt $E_h = -0{\cdot}308$,,
$\mathrm{Fe}/n\ \mathrm{Fe}^{\cdot\cdot}$ salt $E_h = +0{\cdot}340$,,

This process was modified by Wannschaft[95] in that the roasted ore was treated with chlorine after being ground with a calcium chloride solution, a further quantity of ground ore being added when the solution is heated to 60° to 70° C. The iron in solution is removed as ferric hydroxide by agitation with air, and the liquid after filtration contains about 100 gms. of nickel per litre as $\mathrm{NiCl_2}$. Nickel sheet cathodes and carbon anodes are employed with a current density of 1–1·2 amps. per 100 sq. cm., and 4–4·5 volts per cell, a current efficiency of 93 per cent. is stated to have been obtained. The chlorine liberated at the anodes was collected by means of hoods. Analyses of the deposited nickel showed only traces of impurities, 0·06 per cent. Fe, 0·02 per cent. Cu, and 0·02 per cent. SiO_2. It is stated that crude nickel copper alloys obtained by desulphurization of the sulphides can be successfully refined in an acid copper sulphate electrolyte maintained at 30° C. After the copper is removed nickel can be recovered by electrolysis at a higher applied E.M.F. with insoluble anodes. Details of these processes are, however, lacking.

The Electrolytic Refining and Plating of Nickel.—It has already been indicated that practically complete separation of nickel from copper can be obtained by careful adjustment of the cathode potential. The electrolytes favourable for the deposition of copper are, however, not those from which nickel can be deposited successfully.

Since the cathodic potential of nickel in a normal nickelic salt solution is $+0{\cdot}228$ volt, it follows that hydrogen would be more easily liberated than nickel out of even a moderately acid solution. The difficulty is further emphasized by the fact that the overpotential of hydrogen on nickel is low according to Caspari, less than 0·20 volt, and that the velocity of reaction—

$$\mathrm{Ni}^{\cdot\cdot} \rightleftarrows \mathrm{Ni} + 2\oplus$$

is very slow.[96] Nickel and iron have a marked tendency to become anodically and cathodically passive, thus necessitating an increased cathodic polarization. With a working current density of 1·0 amperes per 100 sq. cm. a cathode potential difference of $-0{\cdot}64$ volt was found necessary. It follows that a nearly neutral solution for the electrolyte is most desirable, provided that the formation of basic salts is avoided. In common with other metals that easily become passive, such as gold in a chloride solution and iron, the velocity of solution of the nickel anode and of deposition of metallic nickel from the ionic condition are greatly accelerated by rise in temperature.[97] Accordingly the best conditions for deposition are found at relatively high temperatures, viz. 60°–70° C., at a high concentration of nickel ions, and a solution as nearly alkaline as can be conveniently managed without the deposition of basic salts.

Nickel Plating.—The advantages to be obtained by a fine deposit of adherent and dense nickel on metals are partly negatived by the difficulties inherent in the methods of electrodeposition employed. The inclusion of relatively large quantities of hydrogen and probably small quantities of iron[98] cause the deposited nickel to become brittle and hard and exhibit a great tendency to peel. Better deposits may be obtained at high temperatures.

Nickel does not give a satisfactory deposit on zinc or tin unless a "Striking" bath is employed, more commonly a thin deposit of copper is first formed before the nickel is plated on. Cast nickel anodes are preferable to rolled or electrolytic nickel in the usual electrolytic deposition baths, since they exhibit only a small tendency to exhibit passivity phenomena; this may be counteracted by the addition of small quantity of nickel chloride to the bath or by the use of chloride electrolytes. When thick deposits are required the nickel plating bath must be run warm about 70° C., but for ordinary thin deposits room temperature is usually maintained. Of the various electrolytes suggested for the deposition of the nickel the following have been shown to be most successful.

Sulphate Electrolytes.—Brochet modified Pfanhauser's solution[99] for the composition of a nickel ammonium electrolyte—

Nickel sulphate, 166 gms. per litre.
Nickel ammonium sulphate, 55 gms. per litre.

The electrolyte is conveniently operated at room temperature with a current density of 0·3 ampere per 100 sq. cm. The alkalinity of the bath decreases when relatively insoluble anodes are employed, and must be corrected. A hard good deposit is obtained suitable for iron or steel. A softer and thicker deposit may be obtained by substituting ammonium citrate or tartarate for the nickel sulphate in the above electrolyte.

Chloride Electrolytes.—Nickel chloride (15 gms. per litre) gives an unsatisfactory deposit unless converted into the double salt nickel ammonium chloride when deposits equal to those obtained from the double sulphate electrolyte may be obtained. Dechert has suggested the use of calcium chloride as a substitute for the addition of ammonium chloride.

Other acid complex electrolytes have been used from time to time. Pott's electrolyte containing nickel acetate (20 gms. per litre), calcium acetate (16 gms. per litre) and glacial acetic acid (3 gms. per litre), is stated to be an excellent electrolyte for the deposition of the metal.

Pfanhauser and Langbein both recommend the addition of boric or citric acid to the double sulphate electrolyte, whilst Powell [100] suggested benzoic acid.

Nickel ethyl sulphate,[101] nickel phosphate with sodium pyrophosphate,[102] nickel fluosilicate with aluminium fluosilicate, and ammonium fluoride[103] are found among the more recent patents in various dilutions as suitable electrolytes for the deposition of dense and smooth deposits on zinc or brass.

It is claimed that malleable nickel may be deposited from either of the following electrolytes [104] :—

(1) 8 per cent. nickel as nickel fluoborate.
(2) $NiCl_2$ 5 per cent. ; nickel borate 2 per cent.

It will be noted that only very weak acids are suitable as addition agents and that the best deposits are obtained from very nearly neutral electrolytes.

Alkaline Electrolytes.—A few suggested electrolytes contain nickel as the complex ion $Ni(NH_3)^{\cdot\cdot}_4$, amongst which may be mentioned—

1. Desmur's solution—

Nickel ammonium sulphate	7	gms. per litre.
Sodium bicarbonate	8	,, ,,

2. Bischof's solution—

Nickel sulphate	86	,, ,,
Ammonium sulphate	17	,, ,,
Ammonia (0·880)	120	,, ,,

The complex cyanide solutions have proved unsatisfactory for nickel deposition. Certain organic addition agents have been recommended for ensuring smooth even deposits. Tannin, gelatine, glue, certain glucosides and glycerine have all been the subject of patent literature.

COBALT.

The electrolytic preparation or refining of cobalt from its ores has not been the subject of technical investigations. Doubtless, methods applicable to the deposition of nickel could be adapted to suit this metal on account of their close similarity; the electrolytic potential of cobalt $E_h = +0{\cdot}232$ being only $+0{\cdot}004$ volt higher than that of nickel. Owing to the lack of demand for this element the price rules higher than that for nickel, although the available supplies are large.

Recently, experiments on electroplating with cobalt have indicated that this metal apparently offers some advantages over nickel deposits. O. P. Watts [105] has summarized the somewhat conflicting evidence in respect to the merits of the two metals. Kalmus, Harper and Savell,[106] as a result of a long series of technical experiments, came to the conclusion that cobalt plating was superior to nickel for the following reasons :—

(1) Cobalt ammonium sulphate is 2·5 times as soluble as nickel ammonium sulphate, thus permitting of a greater speed of electroplating with the same applied E.M.F.

(2) The cobalt film was strongly adherent and hard on both brass and iron.

(3) A current up to 4 amperes per sq. dm. can be employed continuously in cobalt plating baths which is over three times the current density permissible with nickel. In one electrolyte a current density of 26·4 amperes per sq. dm. was used for a short period, and produced a satisfactory deposit.

(4) The deposited cobalt is harder than nickel, it takes a high polish showing a beautiful white lustre with a slightly

bluish tint. The actual weight of hard metallic cobalt is computed to give the same protection as 4 times its weight of the softer nickel.

(5) Both cast and rolled cobalt anodes may be used; passivity phenomena do not appear to be so much in evidence in the electrolytes employed by these investigators.

(6) Plates up to any desirable thickness may be deposited.

(7) Current efficiencies of nearly 100 per cent. could be obtained with current densities up to and over 5 amperes per sq. dm.

The two most satisfactory electrolytes were found in baths of the following compositions:—

(1) Cobalt ammonium sulphate (cryst), 200 gms. per litre.

(2) Cobalt sulphate, 312 gms. per litre.
Sodium chloride, 19·6 „ „
Boric acid, nearly to saturation.

Cobalt is also probably superior to nickel owing to the fact that hydrogen is much less soluble in the former metal, and we have noted that the peeling properties of metal films can generally be attributed to the solution of this gas in the metal.

The cobalt ammonia electrolytes containing the complex ion $Co(NH)_3)^{\cdot\cdot}{}_4$, suggested by Boettger, Beardslee, and others, have not proved satisfactory in practice.

The double sulphate bath mentioned above has been modified by the addition of magnesium sulphate with or without a small quantity of citric acid.

In practice the use of baths weaker than (1) and (2) would be indicated owing to the unavoidable loss of solution on removing the plating articles. Langbein suggests as a depositing bath suitable for electrolysis—

Cobalt ammonium sulphate	40 gms. per litre.
Boric acid	20 „ „

Deposition of Cobalt Nickel Alloys.—O. P. Watts gives the composition of a bath from which it is claimed the hardest alloy of nickel and cobalt can be deposited (75 per cent. Ni : 25 per cent. Co)—

Nickel ammonium sulphate	147 gms. per litre.
Cobalt ammonium sulphate	40 „ „
Ammonium sulphate	56 „ „

Langbein suggests the addition of boric acid.[107]

Deposition of the two metals from such solutions in the ratio of 3 Ni to 1 Co can undoubtedly be obtained, anodic solution of the two metals must, however, be in the corresponding ratio. There are two alternative schemes by which this could be accomplished, either by the insertion of two electrodes, one nickel and the other cobalt, and passing the correct current for dissolution through each electrode, or by the casting of an alloyed anode. The nickel cobalt anode would probably dissolve with perfect uniformity, since the metals are miscible in all proportions in solid solution.

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SECTION II.—ELECTROLYSIS IN FUSED ELECTROLYTES

SODIUM.

PRACTICALLY all the sodium produced at the present time is made by electrolysis of fused caustic soda, although

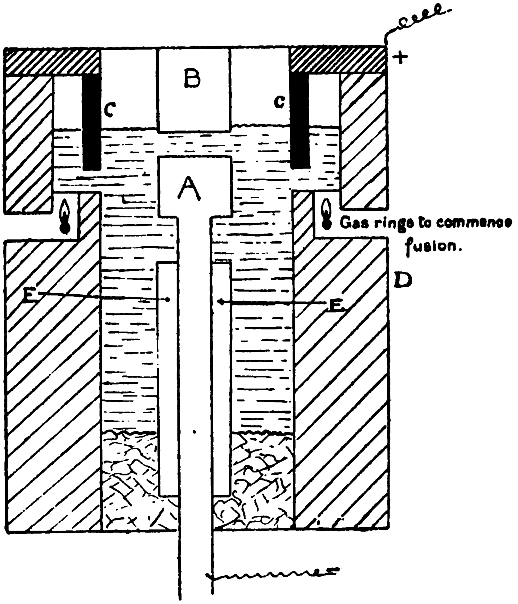

FIG. 7.—Castner cell for electrolysis of fused caustic soda.

attempts to use sodium chloride as electrolyte have been partially successful.

The Castner Process.—The Castner cell (Fig. 7) consists of a cast-iron vessel, D, into which an iron cathode, A, is luted by fused caustic soda being insulated by a porcelain ring, E. The ring-shaped anode C insulated from the vessel and enclosing the cathode is of nickel and usually perforated to permit of free circulation of the electrolyte. Above the cathode is a ring of nickel wire gauze, B, dipping under the surface of the electrolyte. The sodium liberated at the cathode floats to the top and is retained by the wire-gauze screen. The metal can be ladled out by means of a perforated spoon, or a discharge pipe is fitted to the hood.[1] The largest cells are about 60 cm. deep and 45 cm. diameter, holding about 100 kgm. of molten soda. The cathode current density is about 200 amperes per sq. dcm., and the anode density 170 amps. per sq. dcm. at 5 volts, the total current per cell being 1200 amps., giving a current efficiency of about 45 per cent. The electrolyte is maintained fused by the current, and just sufficient lagging is placed round the cell to ensure the formation of a thin protecting crust of caustic soda and a good seal for the cathode: the cell can be started up by means of a gas burner. Electrolysis is conducted at as low a temperature as possible, 315°–320° C. Above 525° C. the yield is practically zero (m.p. crude NaOH 300° C.), due to the increased diffusivity of the metal in the electrolyte.

The Mechanism of Electrolysis.—Le Blanc and Brode[2] investigated the mechanism of electrolysis and showed that the electrical current efficiency could never exceed 50 per cent. owing to the simultaneous liberation of hydrogen at the cathode according to the equations—

$$2NaOH = 2\dot{Na} + 2OH^{1}$$
$$4OH^{1} \text{ at the anode} \rightarrow 2H_2O + O_2 + 4\ominus$$
$$2H_2O \rightarrow 2H_2 + O_2 \text{ on electrolysis}$$

$$\text{Net reaction } 2NaOH = \overbrace{Na_2 + H_2}\text{ (cathodic)} + O_2.$$

See also V. Hevesy, *Zeit. Elcktrochem.*, **15**, 539; 1909.

Both the liberated sodium at the cathode and the water formed at the anode diffuse through the bulk of the electrolyte and there react, liberating hydrogen; since metallic sodium diffuses more rapidly than water at high temperatures, both hydrogen and oxygen may be liberated in the anode compartment, causing explosions.

Further reactions between the liberated sodium and oxygen resulting from the electrolysis may also account for a small efficiency loss, according to the equation—

$$2Na+O_2=Na_2O_2$$

the peroxide being then again reduced by the sodium at the cathode.

It is evident that as long as the water produced by the electrolysis is not removed from the electrolyte as such, but decomposed into hydrogen and oxygen, the current efficiency can never exceed 50 per cent. Various patents have been taken out to effect this removal, *e.g.* by using a diaphragm unattacked by molten caustic soda to prevent the water returning to the cathode or by passing dry air through the anode compartment, but they have not received technical application.

The decomposition potential of dry fused NaOH, according to Le Blanc,[3] is 2·2 volts. Technical electrolysis is conducted with an applied E.M.F. of 5 volts and a current efficiency of 45 per cent., giving an energy efficiency of 20 per cent.

Hence 1000 k.w. hours are necessary to produce 79 kgm. of sodium.

The Griesheim Process.—In this process the "contact electrode" principle general for production of calcium and strontium, and occasionally used for preparing magnesium, is employed.

A circular iron ring in a shallow bath containing the fused caustic soda serves as anode. The cathode consists of a vertical iron rod which can be lowered by means of gearing to make contact with the electrolyte in the centre of the bath. As fast as the sodium is liberated the cathode is raised and the end of the sodium rod thus formed serves as cathode. A cathode current density as high as 1000 amps. per sq. dcm. is claimed for the process, giving a 35 per cent. current efficiency. The chief advantage of the process lies in the fact that the metal is not so much exposed to the solvent action of the electrolyte as in the Castner process. Against this must be set the very high voltage necessary to operate a contact electrode process with a high cathode current density.

Modifications of the Castner Electrolyte.—Becker[4] suggested the use of a mixture of sodium carbonate and soda as electrolyte in a modified Castner cell, which was provided with a sodium collector above the cathode. The addition of the carbonate to the caustic soda, however, raises the melting-point of the electrolyte; with 50 per cent. carbonate a working temperature of 480° C. is necessary. Under these conditions the yield of sodium is, as to be expected, very small, and no carbon dioxide is evolved at the anode. B. P. Scholl suggested the addition of 50 per cent. sodium sulphide to the fused caustic soda. The theoretical decomposition potential of 2·2 volts for the caustic soda being reduced to 1·8 volts.

The free sulphur liberated anodically reacts with the fused caustic to reform sodium sulphide, which is again electrolyzed.

$$Na_2S = 2\dot{Na} + S''$$
$$4NaOH + 2S = 2Na_2S + 2H_2O + O_2$$

It will be noted that although there is a reduction in the decomposition potential required the fundamental difficulty, viz. the removal of the water, is not accomplished by this means.

There are two other salts utilized for the production of metallic sodium which are worked on a technical scale.

The Darling process (worked at Philadelphia, U.S.A.) is said to employ fused sodium nitrate as electrolyte. The central cathode, stated to be made of carbon, is surrounded by two perforated coaxial metal cylinders, whilst the anode is the cast-iron containing vessel.

With an applied E.M.F. of 15 volts sodium is liberated at the cathode and is there recovered in the usual manner by means of a perforated ladle whilst the anode products from the annular space between the anode and the perforated cylinders are removed and converted into nitric acid by condensation. From the details available of this process it is difficult to find out how the nitric acid is produced by direct condensation, as the anode products would consist entirely of nitrogen dioxide and oxygen :

$$2NO'_3 \rightarrow 2NO_2 + O_2 + 2\ominus$$

The production of nitric acid from this gas mixture by absorption in water would not offer any advantages over the Castner process for making sodium and the usual sulphuric acid nitre process for strong acid. Liquefaction of the nitrogen dioxide (see Partington, "The Alkali Industry") would probably be too expensive even with this concentrated gas. A direct preparation of sodium and nitric acid vapour might be obtained by the regulated admission of superheated steam to the anode compartment, when the following reactions would conceivably take place:—

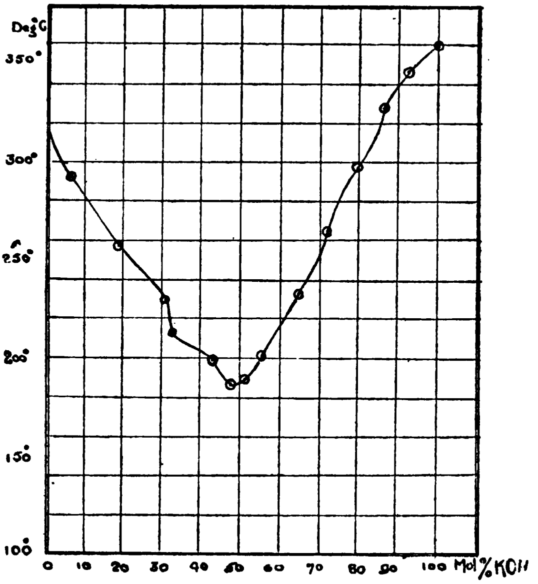

FIG. 8.—Melting-point curve of mixtures of Soda and Potash. (G. v. Hevesy, *Zeit. Phys. Chem.*, **73**, 676.)

$$4NO_3' + 2H_2O = 4HNO_3 + O_2 + 4\ominus$$

If this reaction could be made to proceed smoothly the preparation of sodium and concentrated nitric acid in one operation would prove more economical than the combination of the Castner and sulphuric acid distillation process.

The use of sodium chloride for the production of metallic sodium and chlorine has been frequently attempted. The processes which have arrived at some technical stage in their development may be grouped into three classes.

(A) Processes using direct electrolysis between solid electrodes.

(B) Processes using a molten lead diaphragm serving as intermediary electrode.

(C) Processes using a molten lead cathode.

(A) **Direct Electrolytic Process.**—The preparation of sodium from fused sodium chloride is scarcely feasible on the lines of the Castner or Greisheim process, owing to loss of metal by volatilization, since the m.p. of the electrolyte (crude sodium chloride) lies well above 780° C., whilst the liberated sodium has a boiling point of 877° C., and at 800° C. has already a considerable vapour pressure.

Early experiments by Fischer on a technical scale indicated the conditions necessary for the production of sodium at this temperature. A shallow iron bath divided into two compartments by a vertical partition extending nearly to the bottom of the bath was used as the containing vessel. A horizontal carbon anode was disposed in one compartment and a hollow horizontal metal cathode placed in the other. By maintaining the temperature of the metal electrode below that of the electrolyte, sodium could be drawn off through the tubular orifice. Further investigations showed that an equimolecular mixture of the chlorides of potassium and sodium was more suitable as an electrolyte than the higher melting-point sodium chloride. The resultant sodium contained about 1 per cent. of potassium.

The Virginia Electrolytic Company's process, based on the designs of Seward and V. Kügelgen plant installed at Basel, is practically the only one in successful operation.

A circular furnace CC is employed, lined with firebrick, which is protected by the salt crust EE, and contains a circular graphitic anode BB, with a hollow iron cathode A. The cathode at its upper extremity is surrounded by a water-cooled hood DD. On electrolysis the deposited sodium floats up under the water-cooled hood and flows down through the circular space into the collecting vessel F. A current higher than 200 amps. per sq. dcm. cannot be conveniently used without destruction of the graphite anode. The largest cell constructed on these lines takes about 10,000 amps.

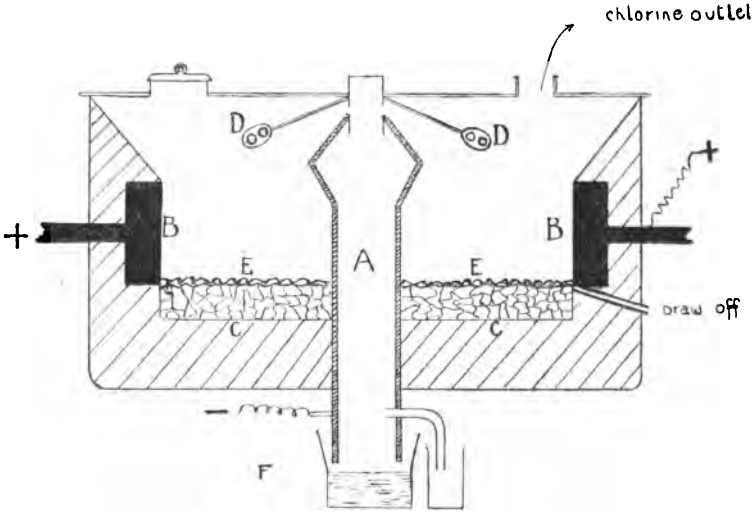

FIG. 9.—Cell for Electrolysis of Fused Sodium Chloride. Virginia Electrolytic Co.'s Process.

(B) Process using a Molten Lead Intermediary Electrode.

The Ashcroft Process[5] is the only one of this type which has been tried on a technical scale. Several unit cells absorbing 2000 to 3000 amps. each have been built, and were stated to function in a satisfactory manner; nevertheless the process is no longer in operation. The mechanism of the cell will be seen from the adjoining sketch. Salt is fed into the cast-iron vessel J, which is provided with an inner lining of magnesia whilst the temperature of the vessel is maintained at 800° C. The cell is provided with a molten lead cathode in the base and a vertical carbon anode F. The molten electrolyte as well as the molten cathode is given a rotational movement by means of the wire helix placed between the magnesia lining and the iron vessel. The whole current operating the cell is passed first through the helix before proceeding to the anode; in this way a vertical electromagnetic force field is generated in the vessel, and since the direction of the current in the electrolyte can be resolved into both a vertical and horizontal component the magnetic field will cut the horizontal current component at right angles, causing a rotational movement of the electrolyte.

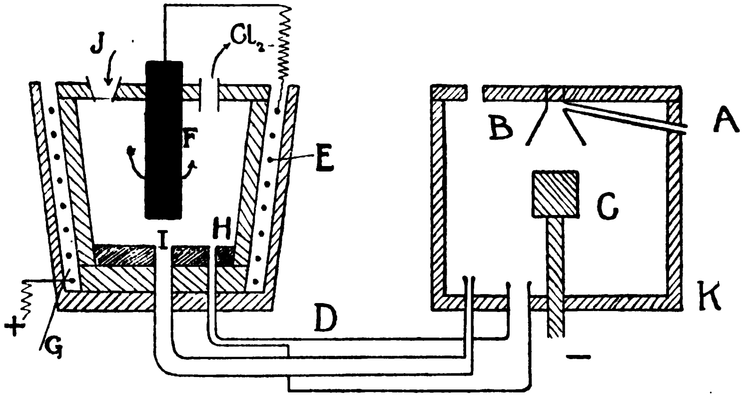

Fig. 10.—Cell for Electrolysis of Fused Sodium Chloride with Intermediary Electrode. Ashcroft Process.

By means of a suitably situated diaphragm the rotating molten lead is caused to flow through the orifice I into the second electrolysis cell K, and return through an annular space surrounding the first tube D back into the vessel through the second orifice H. The tube D thus acts as a heat interchanger for the molten lead; the second electrolytic cell containing fused caustic soda as electrolyte is maintained at 330° C. On passage of the current chlorine is liberated at the anode F, and the lead sodium alloy formed in the first cell is circulated into the second cell, and returned to the first after the sodium has been removed and deposited on the iron cathode C. The molten sodium liberated at C floats up under the hood B, and is drawn off through the overflow pipe A.

The cathode current density is stated to be 200 amps. per sq. dcm. The decomposition voltage of sodium chloride is about 3·0 volts, and should thus be the approximate working voltage of the cell. In practice the whole system requires a P.D. of 9 volts. Seven fall over the NaCl cell and two over the NaOH electrolyte. A current efficiency of 90 per cent. is said to have been obtained, showing an energy efficiency of 30 per cent. 1000 kw. hours would, therefore, produce 85·9 kgm. sodium, a slightly higher yield than obtained by the Castner plant.

Carrier[6] designed a similar cell to the Ashcroft, but took no precautions to work the soda electrolyte at low temperatures. Practically no sodium was deposited at 700° C.

Using a mixture of sodium and potassium chloride as electrolyte in each compartment, it is stated that a fair efficiency was obtained with a voltage drop of 6–8 volts per cell and an anode current density of 20 amps. per dcm.

(C) **Processes using a Molten Lead Cathode.**—The earliest experiments on the technical preparation of sodium were made on these lines, viz. the preparation of a lead sodium alloy and subsequent fractionation to prepare pure sodium. These processes are now no longer used to prepare metallic sodium, but in a modified form, such as the Vautin, Hulin, and Acker, plants have been largely developed to produce caustic soda by treatment of the alloy with steam.[7]

POTASSIUM.

The preparation of potassium from potassium hydroxide can be performed in cells similar to those of the Castner type. Special precautions must, however, be taken to protect the liberated metal from oxidation by immersion in oil.

MAGNESIUM.

Magnesium is prepared by the electrolysis of the fused double salt of magnesium and potassium chloride, carnallite, $KCl.MgCl_2.6H_2O$, obtained from the Stassfurt deposits.

Pure magnesium chloride melts at 710° C., but the double salt is easily fused far below this temperature. In technical operation the electrolyte is maintained between 650° C. and 700° C.

Since molten magnesium is specifically lighter than fused carnallite, it floats to the surface, and has there to be kept separate from the anodically liberated chlorine. This is accomplished by means of a porcelain hood, as indicated in the following sectional diagram. The iron or steel pot C serves as the container protected from the action of the liberated chlorine and from the molten electrolyte by a solidified crust D. The carbon anode A is inserted in a porcelain cylinder open at the bottom and having vertical slits in the part immersed in the electrolyte, whilst an iron cylinder B immersed in the electrolyte serves as the cathode.

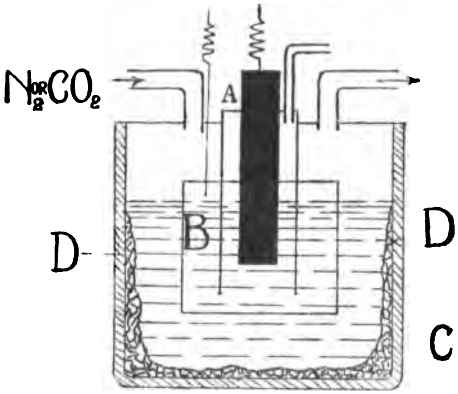

FIG. 11.—Cell for the preparation of the Alkaline Earth Metals from the Fused Salts.

A continuous stream of inert gas (nitrogen or carbon dioxide) is maintained through the upper part of the cell during electrolysis, to sweep out any chlorine which may have penetrated to the cathode compartment.

In practice the temperature is maintained by the electrical energy dissipated in heating the electrolyte. Since the m.p. of magnesium is 633° C. a somewhat narrow range is all that can be permitted in working, and difficulties frequently occur due to solidification of the metal.

Although the decomposition voltage of magnesium chloride is only 3·25 volts, yet in practice from 5 to 6 volts are employed to maintain the temperature of the melt.

If too high voltage be employed an alloy of potassium and magnesium is formed which readily catches fire and causes small explosions in the cell. Traces of iron in the carnallite, a common and nearly unavoidable impurity, lead to inefficient working due to the alternate reduction and oxidation of the iron salt at cathode and anode. Less than 0·1 per cent. of ferric chloride can reduce the current efficiency over 20 per cent. by this means.

Occasionally the small globules of molten magnesium floating to the surface do not coalesce but are again removed into the electrolyte and are carried as a metal fog to the anode, where they are reoxidized. This phenomenon, chiefly due to the formation of a thin oxide film, is caused by using an inert gas containing oxygen in the cell. By the addition of a little calcium fluoride, as suggested by Deville, the oxide film is dissolved and the magnesium will coalesce. A fairly high cathode current density is usually employed from 10 up to 15 amps. per dcm., although A. Oettel[8] has successfully operated a small cell with a current density as high as 40 amps. per sq. dcm. By careful working a very high current efficiency can be maintained, over 90 per cent., and working with a voltage of 5·5 volts per cell the energy efficiency is nearly 52 per cent.; 1000 kw. hours will produce with a 50 per cent. efficiency 70 kgm. of metal.

The Hemelingen Aluminium and Magnesium Works are said to use[9] as electrolyte a mixture of sodium chloride and carnallite in molecular proportions. The process is worked continuously, and the electrolyte is renewed by the frequent addition of anhydrous magnesium chloride. Both the temperatures (750°–800°) and cathode current density (27–30 amps. per sq. dcm.) are higher than usually employed. The current efficiency is stated to be 70 per cent. Attempts have been made to make the process more continuous in its action by reversing the position of anode and cathode in the containing vessel. The iron rod which now serves as cathode is slowly raised from the solution, and the molten magnesium adhering to it solidifies in rod-like form protected by a coat of fused carnallite, the base of which serves as cathode in the electrolyte. The control of the cathodic current density is, however, difficult under these conditions, and a high potassium content in the metal is usually obtained.

Tucker[10] has attempted the electrolysis below the melting point of magnesium at 500° C., when the metal is obtained in the form of a sponge, which can be removed and melted together under a flux of calcium chloride and the electrolyte.

Attempts to deposit magnesium from aqueous electrolytes have proved unsuccessful on account of the high electrolytic solution pressure of the metal $E_h = +1{\cdot}55$ volts. The use of organic solvents for the salts has been the subject of patent literature, but none have proved of practical utility.

CALCIUM.

The preparation of metallic calcium from fused calcium chloride is more difficult than the production of magnesium, although the form of electrolyzer employed is essentially the same in construction.

Pure calcium chloride (m.p. 780° C.) is used as electrolyte, although Ruff and Plato[11] and Wöhler[12] advocated the use of a lower melting point mixture of calcium chloride containing 12 per cent. of calcium fluoride (m.p. 660° C.). Since the melting point of metallic calcium is 800° C. it is possible by maintaining the electrolyte between 780° C. and 800° C. to prepare solid calcium directly by electrolysis. This is accomplished by means of a contact electrode operated in the same manner as described above (1).

Borchers and Stockem,[13] who first produced calcium on a large scale by this method continuously, removed the calcium and immersed it in petroleum to quench it, whence a porous residue containing 50 to 60 per cent. metal was obtained. The metal is fused in a sealed vessel and separated from the adherent chloride.

The decomposition potential of calcium chloride is about 3·25 volts, but in practice very high current densities must be employed, about 10,000 amps. per dcm., necessitating an applied E.M.F. of 20–30 volts.

The tendency to metal fog formation observed in the case of magnesium becomes an important factor in the production of calcium, and only very small yields are obtained unless the contact electrode process of continuous removal be employed.

Laboratory experiments on small units have shown, however, that the preparation of calcium from the fused chloride can be accomplished with much smaller cathode current densities than are stated to be used in technical practice, provided an accurate temperature control is maintained. Frary, Bicknell and Tronson [14] used 9·3 amps. per sq. dcm.; Wöhler,[15] 50 to 250; Goodwin,[16] 3·2 to 20; and K. Arndt,[17] 60.

For economical production the temperature in the neighbourhood of the cathode should just exceed the m.p. of the metal, but the mass of electrolyte should be as much as possible below this temperature, but above the point of fusion of the electrolyte. By maintaining these conditions the deposited calcium can be made to coalesce round the cathode, and may be continuously removed in the form of an irregular rod protected by a layer of fused calcium chloride without a serious loss as metal fog distributed through to the electrolyte. The energy efficiency rarely exceeds 15 per cent. With a 15 per cent. energy efficiency 1000 kw. hours will produce 34·6 kgm. calcium.

Both magnesium and calcium chloride electrolytes suffer from the disadvantage that in the preparation hydrolysis may occur resulting in the formation of a hydroxychloride, which forms an insoluble oxychloride with the liberated metal. This can be avoided in the initial fusion of the chloride by the addition of 15 per cent. ammonium chloride to the moist calcium chloride or carnallite. Regeneration of an electrolyte containing much oxychloride is stated to be impracticable.[18]

STRONTIUM AND BARIUM.

The manufacture of these elements is only conducted on a small scale to meet the requirements of chemical laboratories. The apparatus for their manufacture is, with some slight modifications, similar to those detailed for the manufacture of magnesium and calcium. Strontium and barium do not show such a tendency to produce a fog as calcium, but appear at the cathode as small molten drops of metal which coalesce with difficulty.

LEAD.

Electrolytic lead refining is usually accomplished in an aqueous solution (see p. 83), but Borchers has successfully refined lead from a fused solution of its salts at a high current density and electrical efficiency. Although the direct production of a dense lead without any sponge is a distinct advantage the method has received no encouragement.

The furnace of cast iron is in two parts, separated from one another by a water-cooled insulating joint, which is surrounded and protected by a coating of solidified salt.

The anode side of the electrolytic cell which itself is placed in the flue of an auxiliary furnace is at an angle, its inner surface having a series of deep horizontal platforms which serve to retain some of the crude molten lead fed in from a hopper at the top. A reservoir in the hearth of the cell collects the residues of the lead from where it is continuously run off by means of a syphon. The resultant lead collects in the hearth on the cathode side, whence it is removed by a second syphon.

As electrolyte is employed a mixture of lead oxychloride, potassium and sodium chlorides. The bath is maintained at about 550° C. With an applied E.M.F. of 0·5 volt and a current density of 100 amps. per sq. dcm. 5 kg. of pure lead could be obtained per kw. hour. Betts and Valentine[19] obtained a good electrical efficiency, using molten lead chloride and sodium chloride as electrolyte, adding finely crushed galena from time to time. With an applied E.M.F. of 1 to 1·25 volts good yields of molten lead could be obtained, but the impurities present in the galena soon caused the melting point of the bath to rise above a low red heat, when the process becomes impracticable.

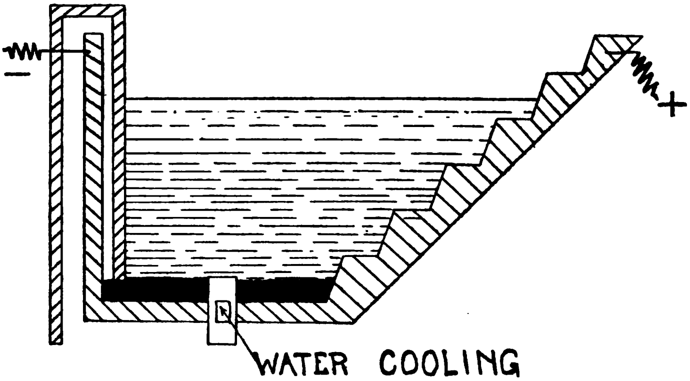

FIG. 12.—Borchers' Cell for refining Lead in Fused Electrolytes.

ZINC.

The preparation of metallic zinc has been accomplished not only by electrolytic processes in aqueous solutions (see p. 58), and by electrothermal methods (see p. 139), but also by electrolysis of fused zinc chloride.

The first semi-technical experiments were conducted by Borchers, who used as electrolytic cell a leaden vessel with a close-fitting lid hermetically sealed in position by fused zinc chloride. As anode a vertical carbon rod was employed, and as cathode a bent piece of strip zinc. Provision was made for recharging and drawing off the liberated chlorine gas. Extraneous heat was required to start the furnace, which was subsequently maintained by the current. In the Ashcroft-Swinburne process zinc chloride produced by the action of dry chlorine on blende at 600° C. to 700° C., after treatment with lead to remove the silver and scrap zinc to remove the lead followed by solution filtration and concentration, is fused in enamelled iron pans [20] to remove most of the water, the rest of the water being removed by a primary-electrolysis between a molten zinc cathode and carbon anodes, as suggested by Lorenz.[21]

The deposition of zinc took place in a firebrick-lined sheet-iron vessel on the base of which molten zinc acted as cathode. Carbon anodes were used and a cast-iron gas-tight roof was employed similar to that used by Borchers. A slight vacuum was maintained to ensure the removal of the chlorine.

When sodium chloride was added to the electrolyte in molecular quantities to the zinc chloride present, a high current efficiency of 98 per cent. was obtained with a voltage drop of 4·5 volts per cell at a temperature of 450° C., and a current of over 3000 amps. or 43 amps. per sq. dcm. of cathode surface. The decomposition potential of zinc chloride is 1·49 volts according to Lorenz,[22] whilst Suchy [23] gives 1·57 to 1·60 volts. Thus the energy efficiency is approximately 35 per cent.; 1000 kw. hours would be necessary to deposit 260 kgm. zinc. When a high temperature is used (600° C. and over, the m.p. of pure zinc chloride is 365° C.), there is a considerable loss of zinc due both to the formation of metal cloud in the electrolyte and also to the volatilization of zinc. This can be much reduced, as noted above, by the addition of potassium or sodium chloride,[24] which also serves to increase the conductibility of the electrolyte. Vogel [25] conducted similar experiments to those of Ashcroft and Swinburne, using fused zinc chloride as electrolyte without the addition of any sodium chloride. He found it impracticable to use a higher current density than 16 amps. per sq. dcm. with an applied E.M.F. of 4·5 volts at 450° C.

The disadvantage of these processes is to be found in the preparation of the fused zinc chloride free from water. Vogel adopted the expedient of evaporation *in vacuo*, whilst, as already indicated, Swinburne removed the last traces by electrolysis using carbon anodes as an oxygen depolarizer. Both methods are exceedingly expensive and somewhat troublesome.

Snyder[26] suggested that in the direct fusion of blende with carbon and iron-lime fluxes in a d.c. furnace partial reduction by electrolytic means takes place, resulting in the formation of zinc at one electrode and carbon disulphide at the other. The distinction between electrothermal and electrolytic reduction is, however, by no means clear in those cases where carbon is added to the melt.

ALUMINIUM.

The only commercial process for the extraction of aluminium from its ores is the thermal electrolytic method introduced by Hall in America and Héroult on the Continent in the year 1887. Although aluminium in the form of complex silicates forms a great portion of the earth's crust, clays containing some 15 per cent. of aluminium, yet the economic production of the metal from these sources is at present an unsolved problem.

The chief raw material is bauxite, obtained in large quantities from Ireland (Larne), France (Rhône Valley), and North America (Alabama), and cryolite obtained from Greenland.

The composition of bauxite varies with the source; the following represent typical analyses :—

Per cent.	Irish.	French.	American.	Austrian.
Al_2O_3	56	60	59	54·1
Fe_2O_3	3	22	2	10·4
$S.O_2$	12	3	3	1·20
TiO_2	3	3	4	—
Water and volatile matter	26	12	32	21·9

For the production of pure aluminium the impurities in the bauxite have first to be removed. There are three processes of purification which have received technical application. In Hall's process (1901) the bauxite is first calcined mixed with 10 per cent. of carbon, and fused in a carbon-lined electric furnace. If the iron content is too low more is added, and the easily reducible impurities are removed by settling to the bottom as a metallic alloy. The alumina resulting from the purification of the bauxite is, however, not so suitable as alumina prepared by the wet processes, since owing to the high temperature employed (m.p. Al_2O_3 2000° C.) the alumina is prepared in a form which does not easily dissolve in the electrolyte employed for the production of aluminium. The addition of metallic aluminium powder has been suggested for the reduction of the impurities instead of carbon.

In the Héroult process the crushed bauxite is gently roasted to remove water and organic matter, then powdered so as to pass a 30-mesh screen. The powdered material is digested with caustic soda solution, sp. gr. 1·45, under a pressure of 6 atmospheres for three hours, during which period the aluminium passes into solution as sodium aluminate. After filtration through wood pulp filters into lead-lined vats, the alumina is reprecipitated by carbon dioxide. Silica is also thrown down in the process, and since the alkali is converted into carbonate it has to be recausticized. Bayer modified this process to overcome these objections by adding to the sodium aluminate solution some precipitated aluminium hydroxide made in a previous operation, when, after 36 hours under agitation, about 70 per cent. of the dissolved aluminium hydroxide can be recovered. The alumina is washed, dried and finally roasted to about 1100° C. to render it non-hygroscopic, whilst the soda solution, after concentration in a triple-effect vacuum evaporator, is utilized for extraction of a fresh quantity of bauxite. Over 40 per cent. of the cost of manufacturing aluminium is stated to be found in the purification of the bauxite.

The electrolyte consists essentially of a solution of alumina in fused cryolite ($AlF_3.3NaF$), with or without the addition of a variable amount of sodium fluoride, calcium fluoride, aluminium fluoride, and occasionally small quantities of the chlorides of sodium or calcium.

In the Hall process the electrolyte is prepared by treating a mixture of alumina, cryolite, and fluorspar with hydrofluoric acid in a lead-lined vat. After drying, the mass of mixed fluorides is melted in the electrolytic smelting furnaces.

It is stated that the electrolytes used in the Hall and Héroult processes have the following components :—

Per cent.	Hall.	Per cent.	Héroult.
AlF_3 ..	59·0 per cent.	$AlF_3 3NaF$ ..	28·0 per cent.
NaF ...	21·0	CaF_2*.. ..	15·6
CaF_2 ..	20·0	AlF_3	56·4

These electrolytes dissolve some 20 per cent. Al_2O_3 at the temperatures employed.

The Hall furnaces are of cast iron lined with carbon, and at Lockport, N.Y., are some 1 metre long by 180 cms. wide, and 1 metre deep. The carbon liner serves as cathode, whilst a number of carbon rods 44 sq. cms. in cross-section, mounted in a special holder, some 40 to the holder and four holders to each bath, serve as anodes.

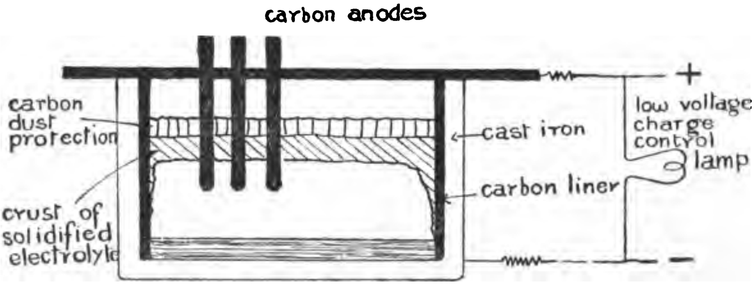

FIG. 13.—Hall Furnace for the Electrolytic Production of Aluminium.

The furnaces are worked in series, each anode taking 250 amps. The total current being nearly 10,000 amps. represents a cathode current density of 100 amps. per sq. dcm., and at the temperature of working (below 980° C.) the applied E.M.F. per cell is approximately 5·5 volts. Aluminium is regularly deposited on the carbon base and

---

* With an addition of from 3 to 4 per cent. of calcium chloride.

serves as cathode, being in contact with the carbon, whilst the anodic oxygen liberated by the reaction—

$$2Al_2O_3 \rightarrow 4Al + 3O_2$$

consumes the carbon anodes according to the equation—

$$Al_2O_3 + 3C = 2Al + 3CO$$

which have to be maintained less than two inches from the molten aluminium. The furnaces are tapped once a day. The removal of alumina from the electrolyte is accompanied by a rise in voltage across the electrodes, indicated by the luminescence of a low-voltage lamp shunted across the bath terminals. Fresh alumina is continuously fed in to maintain as low a voltage as is convenient.

According to Pring[27] about one-half of the energy is expended in the chemical work of decomposing the alumina, and the remainder is converted into heat which serves to keep the bath at the proper temperature.

To maintain the temperature the surface of the electrolyte, which is usually solid owing to the formation of a thick crust, is covered with a layer of powdered carbon or granulated charcoal. This also serves to obviate the burning away of the anode electrodes at the point where they enter the electrolyte by maintaining a reducing atmosphere of carbon monoxide. Whitewashing the anodes has also been suggested as a good remedy for this trouble.

The original Hall furnaces were externally heated, but this method of procedure has now been dispensed with. Not only is the internal electric heating more economical, but the iron vessel is protected from attack by the formation of a crust of electrolyte on the cooler surfaces.

The Héroult furnaces are on similar designs to the Hall, and are made either round or rectangular in section. Carbon cathodes in an iron containing vessel are employed; the anodes, however, are usually stouter, occasionally up to 35·5 cms. in diameter. Special precautions are taken in the Héroult design to make use of the protecting crust of solidified electrolyte.

Working Temperature.—The working voltage is about 7·0 with a cathode current density of 190 amps. per sq. dcm. A considerable divergence is found amongst the published figures for the operating temperature of the cryolite electrolytes. The usual temperature is in the neighbourhood of 800° C., but temperatures as high as 1000° C. and as low as 750° C. have been employed.

Cryolite melts at 1000° C.[28] The melting point is first lowered and then raised by the addition of alumina, as is indicated by the temperature composition diagram.

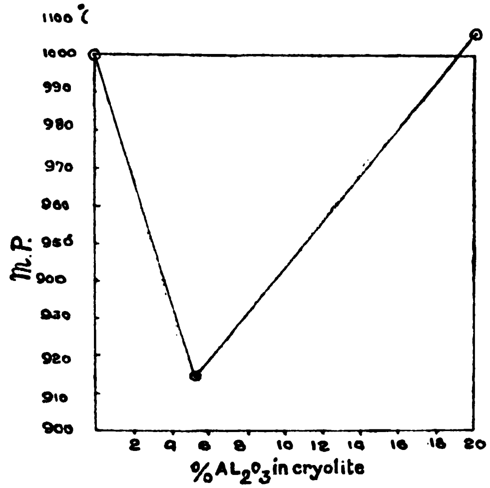

FIG. 14.—Melting-point composition diagram for alumina dissolved in cryolite.

To obtain low temperature electrolytes the addition of other substances is necessary, as has already been mentioned. The electrolyte $2(AlF_3 3NaF)3CaF_2$ is said to have an m.p. of 820° C., whilst the addition of the somewhat volatile sodium chloride lowers the m.p. to under 710° C. When it is remembered that the m.p. of aluminium is 657° and the b.p. 1800° C.,[29] the importance of working at a low temperature will be obvious.

If too high a cathode density be employed the efficiency falls off owing to the resolution of aluminium in the electrolyte due to the formation of metal fog; furthermore, the deposited metal may contain traces of calcium and sodium formed by electrolysis of the calcium and sodium fluoride present. The following figures by W. Richards [30] indicate how closely the molten metal approximates in density to the electrolyte; when solid the specific gravity of electrolyte is actually greater than that of the metal :—

	Specific gravity.	
	Solid.	Fused.
Aluminium, commercial	2·66	2·54
Cryolite	2·92	2·08
Cryolite saturated with Al_2O_3	2·90	2·35
Cryolite and aluminium fluoride, $AlF_3 3NaF + 2AlF_3$	2·96	1·97
Cryolite and aluminium fluoride saturated with alumina	2·98	2·14

In practice it is found advisable not to add too much sodium fluoride, since although this lowers the melting point yet it increases the solubility of the aluminium, and arc formation may occur. Aluminium fluoride also lowers the melting point, but it raises the sp. gr. of the melt; its addition should therefore be controlled. Calcium fluoride [31] appears to be the best addition substance, as it forms a eutectic at 815° C. with 37 mols. per cent. of AlF_3.

Current Efficiency.—The actual decomposition voltages of the various salts comprising the electrolyte are not accurately known. Experiments made by G. Gin and Minet [32] generally confirm the figures of Richards and Minet arrived at by calculation.

	Decomposition Voltages calculated.			
Salt.	Gin.	Richards.	Observed value.	Calculated value assuming complete anodic depolarization.
Al_2O_3 ..	2·79	2·8	2·3	2·2
AlF_3 ..	3·93	4·0	2·49	2·50 $\left\{\begin{array}{l} C+4F' \\ =CF_4+4\Theta \end{array}\right\}$
NaF ...	4·7		—	—

$$E_h(Al)/nAl_2(SO_4)_3 = +1{\cdot}28 \text{ volts.}$$

The current efficiency of a furnace operating at a temperature of 900° C. is about 65 per cent. An increased efficiency results in lowering the temperature owing to the reduction in the formation of metal fog. At 750° C. a current efficiency of 95 per cent. has frequently been obtained. It will be noticed that the energy efficiency of the furnace is low; assuming the best working conditions are maintained with a 95 per cent. current efficiency and 5·5 volts per furnace, the energy efficiency is only

$$95 \times \frac{2{\cdot}2}{5{\cdot}5} = 38 \text{ per cent.}$$

With 100 per cent. energy efficiency 1000 kw. hours would produce 153·2 kgm. of metal; in most works the output is approximately 25 kgm. per 1000 kw. hours.

Anode Consumption.—It has already been noted that practically complete anodic depolarization is obtained by the liberated oxygen consuming the anodes, forming carbon monoxide and with high current densities a mixture of carbon monoxide and dioxide according to the equations—

$$Al_2O_3 + 3C = 2Al + 3CO$$
$$2Al_2O_3 + 3C = 4Al + 3CO_2$$

When the voltage of the bath is allowed to rise owing to lack of dissolved alumina, anode effects may occur due to the liberation of halogens, either fluorine or chlorine if sodium chloride be present in the electrolyte. Halogen depolarization is also complete at this temperature, resulting in the formation of CF_4 or CCl_4. For every kilogramme of metal produced the consumption of carbon electrode is roughly 0·6 kgm. from this cause alone. The electrodes must be maintained within two inches of the molten metal in order to reduce the resistance voltage loss over the furnace; this can only be accomplished by regulating the distance by observation of the ammeter and voltmeter. Frequently internal arcing is caused, accompanied by an increased electrode loss.

If the anodes are not thickly protected by whitewash they are occasionally oxidized by the air at the point where they enter the crust of molten electrolyte, and long pieces of carbon drop into the bath. These additional losses bring the electrode loss up to nearly weight for weight with the aluminium deposited, although with careful working the former figure of 0·6 kgm. per kgm. metal can be obtained. The anode carbon must be of high grade to prevent undue contamination of the aluminium with iron. Technical working anode current densities vary from 80 amps. per 100 sq. dcm. in the Héroult to over 400 in the Hall. Blount[33] gives the following analysis of commercial aluminium, indicating the high degree of purity actually obtained :—

	I.	II.	III.
Al	99·59	99·00	98·45
Si	0·25	0·87	1·29
Fe	0·16	0·13	0·10

Wright[34] gives the following estimates of costs of production per kgm. aluminium :—

Costs per kgm.

I.	d.	II.	d.
Power	4·8	Power	4·6
Carbon electrodes ..	4·4	Carbon electrodes ..	3·5
Alumina	8·8	Alumina	13·9
Labour, repairs, interest on capital, superintendance	4·4	Miscellaneous ..	1·3
	22·4		23·3

Other electrolytes have been suggested from time to time, but have not received technical application; amongst the more important may be mentioned Al_2S_3 in molten cryolite.[35] The advantages gained owing to the low decomposition voltage of the sulphide (0·90 volt) are more than negatived in practice by the difficulty in preparing the sulphide from bauxite. Minet[36] used a solution of cryolite in sodium chloride.

The annual world's output exceeds some 10,000 tons produced in eleven factories, of which three are in the U.S.A., two in France and Great Britain, and one each in Canada, Switzerland, Austria and Germany.

Aluminium Alloys.

The earlier experiments by Cowles on the electrothermal reduction of alumina by means of carbon in the presence of other metals such as copper led to an extended investigation of the mechanical and chemical properties of aluminium alloys. At the present time there is an increasing demand for a large variety of aluminium containing complexes, and although the Cowles process, which at one period was successful on a technical scale, appears to be no longer in operation, yet it had evident advantages for alloys containing but small quantities of aluminium. A more rigid control over the composition and thermal treatment of the substances is obtained by simple fusion of the required metals.

Amongst the more important alloys may be mentioned—

Alloy.	Percentage composition.						
	Al.	Mg.	Cu.	Ni.	Zn.	Sn.	Cd.
Gold bronze	3–5	—	97–95	—	—	—	—
Steel bronze	8·5	—	91·5	—	—	—	—
Acid bronze	10	—	90	—	—	—	—
Aluminium bronze	96	—	4	—	—	—	—
Duralium ..	79	11	10	—	—	—	—
Magnalium	90–98	10–2	—	—	—	—	—
Argentum ..	7	—	70	23	—	—	—
Rolling alloy	95·5–91	—	3–4	1·5–5	—	—	—
Casting alloy	75	—	6	2	—	5	12
Improved brass	2·5	—	70	—	27·5	—	—
Optical instrument alloy	90·5	—	—	—	—	9·5	—

"Tiers argent" 66 with 33 per cent. of silver.

The wide application of aluminium alloys for technical purposes is the subject matter of the VIIIth and IXth Reports of the Alloys Research Committee of the Institute of Mechanical Engineering, in which the chemical, physical and mechanical properties of a very large number of industrial alloys are dealt with.

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SECTION III.—THE ELECTROLYTIC PREPARATION OF THE RARER METALS

GALLIUM.

GALLIUM is conveniently deposited on a platinum cathode from the complex gallate formed on solution of a gallium salt in excess caustic soda. The deposit can be melted off the cathode under warm water (m.p. 30·15°, but can be supercooled to 0° C.).

INDIUM.

According to Schucht[1] the neutral sulphate is the most suitable electrolyte to use. Dennis and Geer[2] suggest the nitrate or chloride, with the addition of a reducing agent such as formic acid. Thiel[3] suggests a weakly acid bath containing sulphuric acid and ammonium sulphate. The electrolytic potential of indium is approximately $E_h = +0{\cdot}45$ volt, and resembles cadmium.

THALLIUM.

Lepième in 1893 suggested the double oxalate of ammonium and thallium as a suitable electrolyte. Förster made use of a neutral sulphate electrolyte, deposition taking place on a copper cathode of 100 sq. dcm., using a platinum anode of 8 sq. cm. and a current of 1·3 to 1·5 amps. at 35 volts. The metal can be fused under KCN. Partial precipitation on the anode as Tl_2O_3 is liable to occur, especially in the presence of reducing agents such as acetone.

The electrolytic potential of thallium is approximately $E_h = +0{\cdot}322$ volt (for $Tl/Tl^{\cdot}$ solutions), the metal thus resembling cobalt or iron. The reducing power of the thallium salts in terms of the electrolytic potential difference $Tl^{\cdots}/Tl^{\cdot}$ is—

$$E_h = 1{\cdot}199 + 0{\cdot}024 \log_e \frac{Tl^{\cdots}}{Tl^{\cdot}} \text{ volts.}$$

Fused Electrolytes.—The elements cerium, neodymium, praseodymium, lanthanum and samarium are most conveniently prepared by electrolysis of the fused anhydrous chlorides. They are all white metals with a slightly yellowish tinge and fairly stable in air, lanthanum being the most easily oxidized.

The temperature necessary for electrolysis varies for each metal, as seen from the following table :—

	M.p. metal.	Fusion point of chlorides.
Ce	625° C.	—
La	810°	907°
Nd	840°	785°
Pr	940°	818°
Sm	1300°–1400°	686°

Hildebrand and Norton advised the use of iron electrodes ; the cathode being placed in a porous porcelain cell containing the fused chloride, protected by a layer of ammonium chloride. In the anode compartment surrounding the porcelain cell a mixture of fused sodium and potassium chloride was used.

Muthmann advocated the use of a water-cooled copper electrolytic cell containing two vertically situated carbon electrodes. As electrolyte he used the fused chlorides, with or without the addition of the chlorides of sodium, potassium and barium. He recommends the following electrolyte for cerium :—

$CeCl_2$	200 parts.
NaCl.KCl	15–20 parts.
$BaCl_2$	A trace.

Electrolysis with a current of 120 amps. at 12–15 volts yielded 750 gms. of metallic cerium in 6 hours.

With samarium a very high cathode current density is required to ensure the fusion of the metal. The addition of $\frac{1}{3}$ part by weight of barium chloride to the chloride is advised.

BORON.

Experiments by Hampe[4] on the electrolysis of molten borax indicated the formation of a sodium boron alloy at the cathode. Lyons and Broadrill,[5] using a fused borate electrolyte and a carbon anode, claim the preparation of boron by reduction of the B_2O_3.

The carbides B_2C_2, B_6C, are the products of electrothermal reduction (see p. 172).

VANADIUM.

M. Gin[6] suggested the electrolysis of molten vanadium fluoride between an iron cathode and a compressed mixture of carbon and vanadium trioxide as anode material in a cell lined with alumina. With a cathode current density of 600 amps. per dcm. and an anodic one of 200 amps. per dcm. and an E.M.F. of 11–12 volts, pure vanadium could be deposited on the cathode with the reformation of vanadium fluoride at the anode—

$$2VF_3 = 2V + 3F_2$$
$$3F_2 + V_2O_3 + 3C = 2VF_3 + 3CO$$

An alternative method is the use of a carbon anode in an electrolyte of V_2O_3 dissolved in a double fluoride, $2VF_3.3CaF_2$.

Wood's process entails the use of the oxide and calcium oxide as electrolyte, requiring a much higher temperature.

TITANIUM.

Borchers[7] patented the use of calcium chloride as electrolyte with the continuous addition of titanium dioxide for the preparation of the pure metal.

Pederson[8] suggests copper titanium as an industrial alloy suitable for many purposes; it is prepared by the electrolysis of titanium dioxide in calcium fluoride as electrolyte, using a copper cathode.

MANGANESE.

Experiments by Guntz [9] and Bunsen [10] on the electrolysis of concentrated solutions of manganous chloride indicated that the preparation of the metal free from all traces of oxide was a matter of great difficulty. Better results are obtained by electrolysis of the fused chloride or fluoride in an alkali chloride electrolyte. Simon [11] suggests calcium fluoride as electrolyte, adding manganese oxide continuously to the electrolyte in a manner similar to that adopted in the production of aluminium.

URANIUM.

This can most conveniently be prepared by electrothermal methods (see p. 153), but very pure metal can be deposited by electrolysis of the fused chloride UCl_4 between carbon electrodes.[12]

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SECTION IV.—ELECTROTHERMAL PROCESSES

ZINC.

WE have already referred to the electrolytic deposition of zinc in both aqueous and in fused solutions, but the most serious rival to the ordinary Belgian thermal practice is to be found in the electrothermal processes. The ordinary method of smelting zinc suffers from serious disadvantages. In general practice the ore, after roasting to convert the sulphide or carbonate into the oxide, is mixed with about half its weight of coal slack or coke, and heated in small fireclay retorts. Owing to the high temperature necessary to expel the zinc (over 1100° C.) the retorts must be small, holding only some 30–40 kgms. of the charge: the distillation of the zinc is completed in 20 hours. With a high-grade ore one and a half tons of coal per ton of ore is the minimum consumption, whilst even 4 tons of coal per ton of ore may be required in a badly operated furnace with a low-grade ore. The life of a retort is short, averaging from 30 to 40 days, being attacked not only by the hot gases outside and the zinc vapour inside, but also by the slags, especially by those with a high lime or iron content. J. W. Richards [1] has calculated the thermal efficiency of the average furnace to be under 7 per cent.* The process is further complicated by the difficulty of removal of the infusible slags remaining in the retorts.

Not only are the furnace operation costs high in both labour and material, but great difficulties are met with in

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* For information on the thermal conductivities of various furnace liners, as well as the heat loss from furnaces and electrodes of different shapes and sizes, see Northrup, McLeod, Kanolt, Fitzgerald, Langmuir, and others in *Trans. Amer. Electrochem. Soc.*, 1912 to 1917; also Bronn, "Der Elektrische Ofen."

the condensation of the zinc vapour. There is a substantial loss due to diffusion of the vapour through the walls of the retort and to the retention of part of the zinc in the slag, especially if the sulphur has not been entirely eliminated by roasting. Again, in the actual process of condensation of the zinc only a part coalesces to a regulus " spelter," the remainder being recovered as " blue powder."

The formation of " blue powder " is more common in electrothermal processes than in the Belgian, but is by no means an unimportant factor in the latter.

There are three factors which are considered to have an influence on the formation of " blue powder " :

I. The formation of an electrostatic charge on the zinc vapour globules during the process of condensation.

II. The rapid chilling of the zinc globules in the condenser (the m.p. of the metal being 419° C.). Rapid cooling to, say, 400° C. may considerably undercool the globules before they are run together. Dilute zinc vapour is more liable to be undercooled than more concentrated ones. The optimum condensing temperature has been found to lie between 500° C. and 850° C., depending entirely upon the concentration of the issuing vapour.

III. Superficial coating of the condensing globules with an oxide skin. This factor is probably the most important where very low spelter recoveries are made. Reduction of the zinc oxide may take place according to either of the following equations :—

$$\text{(i)}\quad ZnO + C \lesssim Zn + CO$$
$$\text{(ii)}\quad ZnO + CO \lesssim Zn + CO_2$$

The main reaction following that indicated in the second equation. Owing to the fact that reduction does not proceed with sufficient rapidity under 1100° C., the reduced metal is not removed from the sphere of action by condensation, as is the case with most metals, *e.g.* iron or copper, but remains in the gaseous phase. The reaction is consequently reversible and partial reoxidation of the reduced zinc may take place, especially if the free space between the packed charge and the condenser be too great. The formation of carbon dioxide is usually reduced to as small an extent as possible by addition of excess carbon to the charge, when the resulting gas expelled with the zinc vapour will consist chiefly of carbon monoxide containing but little of the dioxide. The exact ratio $CO : CO_2$ will depend on the temperature of operation, being governed by the equilibrium—

$$\text{(iii)}\quad 2CO \lessgtr C + CO_2$$

The following figures indicate the composition of the equilibrium gas mixtures at various temperatures :—

Temp. °C.	Per cent. CO_2.	Per cent. CO.
450	98	2
550	89·3	10·7
650	61	39
750	25	75
850	6	94
950	1·5	98·5
1050	0·34	99·6

Other gases, such as oxygen, water vapour, hydrocarbons or silicious dust, may all assist in the formation of a film on the condensing zinc globules.

J. Johnson[2] gives the following figures for the vapour pressure of zinc at different temperatures :—

Temp.	Vapour pressure in mm. of mercury.
920° C.	750
750	100
700	50
610	10
500	1
420	10^{-1}
419	m.p.
350	10^{-2}
290	10^{-3}

It will be noted that the vapour pressure of the zinc only becomes small when the gas is cooled to 600° C. Even at this temperature the gas can contain 1·3 per cent. volume of zinc vapour without deposition of any metal, while at the same time over 75 per cent. of the original carbon monoxide has been converted to the dioxide. The effective condensation of zinc can, therefore, never be complete; "blue powder" is always formed, but the quantity can be reduced by the production of a gas rich in zinc vapour and providing a very rapid fall in temperature from 1100° C. to between 600° C. and 700° C. in a very short space. Under these conditions advantage is taken of the relative slowness with which equilibrium will be re-established by cooling to this relatively low temperature according to equations (ii) and (iii).

Instead of redistillation of the "blue powder" alternative treatment by electrolysis in fused or aqueous solution as suggested on p. 59 might prove practicable. If anodic depolarization by means of the free zinc in "the blue powder" (briquetted to anodes) could be made use of, the cost of electrolyte recovery would be reduced to the operation of a refining process.

Power Consumption.—Harbord [3] gives the following figures obtained in test runs at Trollhätten, working with a blende calamine mixture (30 parts Broken Hill ore, 1 part calamine, and 7·5 parts coke dust); the blue powder (containing 54 per cent. zinc and 20 per cent. lead) and oxide recovered from this charge was mixed with a further quantity of blende coke dust and lime, and distilled in a second furnace.

Energy consumption per 1000 kgm. of ore smelted.	Electrode consumption.
2078 kw. hours.	31·5 kgm.

The above figures include the necessary energy for redistillation of the blue powder. Mounden [4] estimates the recovery in these works to be 75 per cent. of the zinc, 80 per cent. of the lead, and 80 per cent. of the silver. Salgues at Ariège, in France, using a 40–45 per cent. zinc ore, obtained 1000 kgm. zinc with a current consumption of 4800 kw. hours, or per 1000 kgm. of ore smelted 2016 kw. hours were required. G. Gin [5] calculates the current of energy required for smelting 1000 kgm. of ore containing 50 per cent. zinc at 1500 kw. hours, while according to Stansfield [6]

Snyder has smelted pure zinc oxide with an energy consumption of 1050 kw. hours per 1000 kgm. of oxide.

Harbord's figure includes the electrical energy consumption necessary for the redistillation of the blue powder, being about 500 to 600 kw. hours per ton of blue powder.

We may take the average power consumption per ton of ore at 1500 kw. hours, as opposed to the maximum and minimum coal consumption of 4 and 1½ tons per ton of ore used in the Belgian process.

Under normal working conditions the electrode loss is estimated at 4*d.* to 6*d.* per ton of ore used, and is thus less costly than the retort consumption of 8*d.* per ton in the Belgian process.

Johnson[7] estimates the electrode consumption at from 1 to 15 kgm. per ton of ore, figures considerably under those obtained by Harbord. It is evident that cheap power rates are essential to the successful operation of electrothermal zinc smelting process.

Types of Zinc Furnaces employed.—The chief advantages to be gained by electrothermal smelting processes is the feasibility of working with charges larger than with the Belgian retorts, and the possibility of continuous operation. Furnaces taking two to three tons per charge have proved satisfactory, while Johnson[8] does not contemplate serious difficulties in operating 10-ton capacity units. Other advantages which become increasingly important when a low-grade zinc ore is used are the possibilities of providing an easily fusible slag which may be tapped off and worked up for valuable metals such as silver and copper, while under certain conditions a molten metal may be run off (especially in ores with a relatively high lead content) in addition to and separate from the slag: conditions scarcely possible in small retorts.

The slag fusion temperature should be adjusted to lie just above the temperature necessary for distillation of the zinc to avoid inclusion of the metal. In silicious slags the addition of silica is the controlling factor, in basic slags carbon.[9]

Resistance Furnaces.—The original application of electrical heating to zinc smelting was made by Cowles in 1880, who adopted a simple form of resistance furnace. In more modern form resistance furnaces designed by Johnson [10] are in use in the United States, and by Salgues [11] at use in Pyrenees and Trollhätten (Sweden, 20,000 kw.), Sarpsborg (3000 kw.) and Hallstahammer in Norway.

The Cowles and the earlier Johnson furnaces were operated with horizontal electrodes inserted in the ends of an arched chamber of firebrick lined with a refractory, such as fireclay or bauxite. The charge containing ore and coke was used as resistance, and the furnaces were intermittent in action. The later forms of the Johnson furnace, as well as those of Salgues, have vertical electrodes and are continuous in operation.

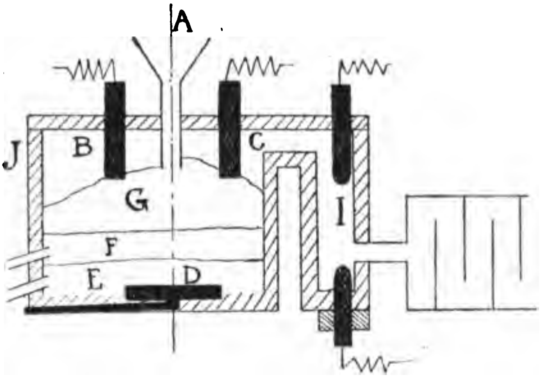

FIG. 15.—Resistance Zinc Furnace. Johnson type.

The roasted ore, mixed with carbon and lime or other flux, is fed in through the hopper A into the smelting chamber J, in which are situated three electrodes B, C, and D. The lower electrode D, a carbon plate, is usually covered with molten lead containing silver (E) when ores containing lead are used; above this is a layer of molten slag F. These two layers have separate tapping holes. The zinc vapour together with a mixture of carbon dioxide and monoxide is passed off to the condenser through the column I, which is filled with broken carbon maintained at 1100° C. By this means pure zinc vapour with carbon monoxide as the only diluent is produced and rapidly condensed in the air-cooled receiver. Johnson has claimed an 80 per cent. zinc and a 60 per cent. spelter recovery from a 30 per cent. ore with this type of furnace.

By introducing the fresh charge under the surface of the slag the production of smoke is said to be minimized, resulting in a decrease of blue powder formation.[12]

Johnson gives [13] the following compositions of the slag and matte tapped :—

Slag analysis.	
SiO_2	40
CaO	22
MgO	2
FeO	10
MnO	1
Al_2O_3	10
ZnO	2
Cu	0·15
Pb	0·05
Ag	0·3 oz./ton.

Matte analysis.	
Fe	45
Cu	25
S	29

For low-grade zinc ores containing relatively large quantities of lead, copper, gold and silver the process offers distinct advantages. The preheating of the charge before introduction into the electric furnace by the gas liberated effects a considerable economy.[14] The resistance furnaces employed at Trolhätten hold each about three tons of charge, and can smelt 2·8 metric tons of ore per 24 hours. A current of 2600 amps. at about 100 volts is used to operate each furnace, corresponding to a current density of 128 amps. per sq. dcm. Two tons of blue powder are re-smelted with every ton of fresh ore. Various modifications have been suggested for the treatment of sulphide ores to overcome the difficulty of the complete removal of the sulphur by prolonged roasting before the reduction. This difficulty can be avoided by the additions of a suitable flux which will remove the sulphur in the slag, such as iron or lime. Snyder [15] suggests treatment of the ore unroasted with iron and with lime fluxes and carbon in a resistance furnace, with the simultaneous production of zinc and carbon disulphide. Brown and Oesterle[16] further improved upon this patent by claiming the simultaneous production of zinc, carbon disulphide and calcium carbide.

The Côte Pierron process[17] uses scrap iron to produce ferrous sulphide according to the reversible equation—

$$Fe + ZnS \rightleftarrows FeS + Zn$$

the equilibrium being shifted over entirely to the right through the volatilization of the zinc out of the liquid phase.

The process is suitable for lead-zinc ores, since the lead can be directly recovered, and the zinc vapour is not diluted with any carbon monoxide. Against these advantages must be set the cost of the scrap iron necessary for reduction, 900 kgm. of iron being required for every 1000 kgm. of zinc and 300 kgm. for every 1000 kg. of lead.

The following costs of production are entailed at Ugine, Savoy.[18] Cost per ton of zinc produced: Power 10*s.* 6*d.*, depreciation 9*s.* 6*d.*, electrodes 4*s.* 6*d.*, iron 3*s.* 4*d.*, labour 6*s.* 6*d.*, miscellaneous 4*s.* 2*d.*; total 38*s.* 6*d.* Eleven per cent. of zinc is lost in the process.

In the Imbert-Fitzgerald furnace[19] wedge-shaped carbon rods are used as a permanent resister for the furnace. A mixture of one part of ferric oxide and three parts of iron sulphide are used as a flux at 1100° C., to which six parts of blende are added; on the addition of molten copper or pig iron the zinc is volatilized off and condensed. The copper, of course, would be recovered from the resulting sulphide in the usual manner, but in practice iron is used. The furnace must naturally be worked in a reducing atmosphere. Dorsemagen suggested the use of a resistance furnace for the production of zinc and carborundum by the reduction of siliceous zinc ores, while Borchers patented a process for the simultaneous production of ferro-silicon and zinc.

The majority of these modified processes in which by-products from the sulphur as carbon disulphide or silica as carborundum or ferrosilicon are obtained have not been worked on a sufficiently large scale to enable an assessment of their technical utility to be made.

Radiation Furnaces.—The most important radiation furnace employed for zinc smelting is that of C. de Laval,[20] which has been used in the United States and also at Trolhätten.

The charge of roasted ore, coke and flux enters through the shaft D, where it is exposed to the radiation from the arc between the horizontal electrodes A. The CO and zinc vapours leave at a high temperature through B to the condenser, while the slag can be removed through the tapping hole C. It will be noted that the arc is operated in a reducing atmosphere which considerably lessens the electrode consumption, although 40 kgm. of electrodes per metric ton of ore are required, a figure considerably higher than given for resistance furnace operations.

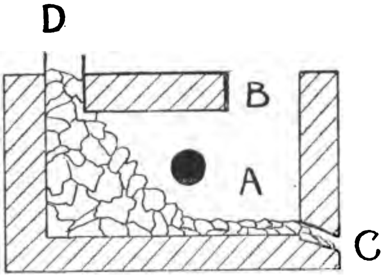

FIG. 16.—Radiation Zinc Furnace. De Laval Type.

Reduction proceeds quietly, and very pure zinc can be obtained in these furnaces, while very little of the metal is retained in the slag. Owing to the low diathermacy of the ore the electrical efficiency is poor, consuming about 70 per cent. more power than the resistance type of furnace. The furnace is very simple to operate.

COPPER.

Very few large-scale experiments have been made in the electrical smelting of copper ore, but some have shown promising results. The treatment for complex copper ores may be roughly divided into three classes :

(A) Ores containing metallic copper (*e.g.* native copper) can be smelted, directly separating the metal from the gangue.

(B) Ores containing copper sulphide or arsenide in addition to iron can be smelted in a blast furnace in which part of the sulphur in the ore is oxidized, the heat of oxidation assisting in the fusion of the ore. The resulting slag should contain the oxides and silica as well as most of the iron, while the matte contains the bulk of the copper as sulphide or arsenide with a small quantity of iron.

(C) Oxidized ores can be selectively reduced with carbon. By careful adjustment of the carbon content in the charge most of the iron can be retained in the slag in an oxidized condition.

Experiments made at La Praz and Livet in France from 1903 to 1907 on the production of copper matte from a sulphide ore in resistance furnaces, were favourably reported on by M. Vattier for the Chilian Government.

The furnace used was a simple resistance one of the Keller type furnished with two pairs of electrodes in separate zones of the furnace chamber, so that the ore fused in one zone could be maintained at the fusion point in the second to effect the separation of slag from matte.

Twenty-four tons per twenty-four hours of ore could be treated in a furnace of 2 cubic metres capacity.

The power consumption was 500 kw. hours per 1000 kgm. ore and 5 kgm. electrode material.

Vattier gives the following percentage analysis of ore, charge, slag and matte :—

	Charge.	Matte.	Slag.
Cu	5·10	47·9	0·10
Fe	28·50	24·3	32·50
Mn	7·64	1·4	8·23
S	4·12	22·96	0·57
Al_2O_3	4·00	0·5	5·20
CaO	7·30	—	9·90
SiO_2	23·70	—	27·20

The power consumption for the furnaces averaged 4750 amps. at 119 volts with a power factor of 0·9.

He calculated that 3·2 metric tons of coke (costing in Chili £13) were required for the ordinary coke furnaces to produce 1 metric ton of copper. The same results could be obtained with 8000 kw. hours of electrical energy. Taking a figure as high as 0·1*d.* per kw. hour, produced by water-power, the power costs would only amount to £3 6*s.*, while the electrode consumption and furnace depreciation would not amount to more than £1 16*s.* per ton of metal produced. Under the conditions where fuel costs are remarkably high, and where electric energy could be produced at very reasonable rates, electrical processes are clearly indicated.

The electrothermal method of copper smelting has been tested both at Kaafjord and Trondjhem, Norway, with success.[21] Experiments in Germany[22] on the reduction of a silicate ore with calcium carbonate and coke at 1600° C., obtained a minimum power consumption of 1100 kw. hours per metric ton, necessitating very cheap water-power. The preparation of copper nickel alloys in an electric furnace has been experimented with in Norway. The process should proceed smoothly owing to the complete miscibility of the metals in each other, forming solid solutions, as indicated in the curve on p. 41.[23] Copper thus prepared is likely to contain cuprous oxide unless a reducing atmosphere is continually maintained in the furnace. Heyn,[24] who had investigated the solubility of Cu_2O in metallic copper, finds a eutectic containing 3·5 per cent. Cu_2O melting some 25° C. below the m.p. of the pure metal.

NICKEL.

W. L. Morrison[25] and S. B. Ladd[26] have described the conditions necessary for the satisfactory smelting of oxidized nickel ores. A small furnace has been worked at Sault St. Marie Ont., U.S.A., while the Consolidated Nickel Co. at Webster have successfully operated on a large scale the reduction of a hydrated magnesium nickel silicate complex containing less than 2 per cent. of nickel.

A resistance furnace of simple type is employed with a carbon hearth and one or a series of vertical electrodes entering through the roof. The ore after crushing is mixed with broken coke, yielding on reduction a nickel ferro-silicon metal of the following composition :—

Ni	14 per cent.
Fe	56 ,,
Si	28 ,,
Other metals	2 ,,

and a slag consisting chiefly of aluminium and magnesium silicate containing about 0·5 per cent. of nickel. The power consumption is about 1200 kw. hours per 1000 kgm. of ore smelted. F. Clergue has suggested the use of a revolving electric radiation furnace for the production of ferro-nickel; his process is said to be in operation at Essen, Germany (see also p. 228).

MANGANESE.

Manganese is usually produced in the forms of spiegeleisen and ferro-manganese, the demand for the pure metal being limited. Although it can be prepared in a pure form by electrolytic methods (p. 138), the electrothermal processes are quicker and more convenient.

Moissan [27] effected the reduction of MnO_2 by carbon in a small arc furnace with a current of 150 amps. at 60 volts, preparing several hundred gms. of the metal in a few minutes. He attempted to remove the excess carbon present in the metal by refusion with MnO_2. Borchers [28] could not confirm the removal of the excess carbon by this method. Gin [29] used a mixture of MnO_2 with sodium sulphate and carbon in a small arc furnace. By this means sodium manganate is produced which has a melting point under 2000° C., from which the manganese can be produced at a temperature well below its point of vaporization (m.p. 1247° C.).

TIN.

Härden [30] has given details of the conditions necessary for the reduction of tin ores. Although electrothermal smelting of tin has not been accomplished on a technical scale, with the exception of tin dross smelting in tin plate works,[31] yet, owing to the unsatisfactory working of the ordinary blast furnace where losses by volatilization of stannic oxide are by no means inconsiderable, the electrothermal methods have some prospect of future development.

CHROMIUM.

Metallic chromium is only prepared on a comparatively small industrial scale, the chief electric furnace production being ferro-chromium (see p. 234). It can be obtained with a simple arc furnace using intermittent charging, the fused metal produced by reduction being broken out. Reduction is usually accomplished by means of carbon according to the equation—

$$Cr_2O_3+3C=2Cr+3CO$$

The reaction commences at 1185° C.[32] The resulting grey metal usually contains the extremely hard carbide, Cr_3C_2, which is difficult to remove.

Refusion with the calculated amount of chromic oxide usually entails the presence of both oxygen and carbon in the metal. More effectual removal can be accomplished by the addition of lime to the charge—

$$3Cr_3C_2+2CaO=9Cr+2CaC_2+2CO$$

although small quantities of calcium chromite are formed under these conditions. Aschermann at Cassel successfully developed a process for the preparation of chromium by reduction with antimony sulphide in a small graphite crucible—

$$2Cr_2O_3+Sb_2S_3=4Cr+2Sb+3SO_2$$

The antimony is entirely removed by reheating. Becket[33] uses silicon as a reducing agent—

$$2Cr_2O_3+3Si=4Cr+3SiO_2$$

MOLYBDENUM.

Metallic molybdenum, for which there is an increasing demand in the production of special steels, is more easily prepared than chromium by the reduction of the oxide with carbon. A small deficit of carbon according to the equation—

$$MoO_2+2C=Mo+2CO$$

ensures the presence of excess oxide in the metal. The oxide is sufficiently volatile to be easily removed by the sublimation from the melt. The most common form of molybdenum ore is the sulphide, and the direct preparation of the metal from molybdenite is the subject of many patents. Guichard[34] and Lehner[35] suggested the reduction with carbon in the presence of lime—

$$MoS_2+2CaO+2C=Mo+2CaS+2CO$$

Becket[36] has claimed the process for reduction with a smaller amount of carbon than indicated by the above equation—

$$2MoS_2+2CaO+3C=2Mo+2CaS+CS_2+2CO$$

Calcium carbonate may, of course, be used instead of lime—

$$2MoS_2+2CaCO_3+5C=2Mo+2CaS+CS_2+6CO$$

The addition of calcium fluoride as a flux causes the reaction to proceed more smoothly.[37] Small traces of iron present in the molybdenite are removed by volatilization on further fusion of the metal. Neumann[38] has suggested the reduction by means of silicon; according to Keeney[39]—

$$MoS_2+Si=Mo+SiS_2$$

unsatisfactory results were obtained. Calcium carbide has a growing market as a reducing agent, and is especially effective for the preparation of metals like molybdenum—

$$5MoS_2+2CaC_2=5Mo+2CaS+4CS_2$$

TUNGSTEN.

This metal is also being used in increasing quantities for the preparation of special steels and in the electric lighting industries. For most steel work the metal is usually not isolated, but reduced to produce ferro-tungsten (see p. 232). Owing, however, to the variable carbon contents of the ferro alloy pure tungsten is used for high-grade steel. In the manufacture of tungsten for steel work and electric lamp filaments the oxide is usually reduced by means of hydrogen in an electric-resistance furnace and subsequently melted to prepare the ductile metal.[40] Metal containing a variable amount of carbon as carbide and free carbon can be prepared in the arc furnace by methods similar to those used for the preparation of chromium.

VANADIUM, TITANIUM AND URANIUM.

These three elements can be prepared by reduction with carbon of their respective oxides, V_2O_5, TiO_2 and U_3O_8. The resulting metals always contain small quantities of the carbides and nitrides.

The industrial demand is in the form of the ferro-alloys, and they are always produced as such.

ZIRCONIUM.

According to Moissan[41] this element can be produced by reduction with carbon with a current of 1000 amperes at 40 volts in a simple arc furnace. Greenwood[42] found that no reduction took place below 1400° C.

The element is not produced industrially.

SILICON.

There is a limited but growing demand for this element as distinct from the ferrosilicon alloy for reduction purposes. Its heat of oxidation, being 215,692 calories per gram molecule, is only exceeded by " thermite " and the alkali metals.

Crude silicon is prepared from silica by reduction with carbon, and in this state it contains SiO_2, N_2, and other impurities. An effective method of purification[43] is to treat the crude material for two hours in a crucible covered with coke, then stir in ½–3 per cent. of magnesium powder. A slag of magnesium silicate is separated, and the silicon can be poured off into sand moulds. Reduction commences at 1460° C., the melting point of the metal being 1430° C. The Acheson Carborundum works[44] use carbon-lined firebrick furnaces with two depending electrodes, the current passing from the electrodes to the hearth. The furnace is operated as a resistance furnace, since the element is volatilized at the temperature of the arc (b.p. 2800° C.). Each furnace uses 1000 kw., and from 250 to 350 kgm. of silicon can be tapped off every few hours.

According to Stansfield[45] a high-grade unrefined silicon had the following composition :—

Si	95·71 per cent.
Fe	2·24 ,,
Al	1·96 ,,
P	0·01 ,,
C	0·08 ,,

Potter[46] has suggested the use of silicon carbide as a reducing agent—

$$SiO_2+2SiC=3Si+2CO$$

Attempts have been made to prepare silicon electrolytically, notably by Deville, Minet and Grosz, using as electrolyte either sodium potassium silicate or potassium silicate, adding silica from time to time; indifferent results were obtained.

A great variety of compounds have been prepared by the interaction of silica and carbon in the electric furnace, some of which have become extremely important in technical work. These will be referred to in a later section (p. 164).

GRAPHITE.

Carbon can exist in at least three well-known modifications, two crystalline[47] and one amorphous: diamond, graphite and ordinary carbon. The diamond is the stable modification at low temperatures, whilst graphite is the stable form above 500° C.

The technical transformation of anthracite, coal or coke into graphite was first developed by E. Acheson. He found that the direct conversion of pure carbon into graphite was a very tedious operation, but that the presence of small quantities of impurities, especially metals such as iron or aluminium and certain non-metals such as silicon and boron, catalytically hastened the conversion.

According to Townsend preliminary ionization is necessary for the formation of graphite from carbon, and the function of the catalytic material apparently serves to produce graphite by the decomposition of a carbide formed by the catalyst with the carbon.

It is assumed that the formation of the carbide takes place in the hottest zone of the furnace, and as the temperature is gradually raised the carbide is decomposed leaving behind graphite, whilst the catalyst is volatilized to the colder zones, there to recommence the conversion of carbon to graphite.

That the presence of a catalyst is not absolutely necessary is shown by the experiments of Acheson, Borchers and others, but for technical production it cannot be dispensed with.

It has already been noted that graphite is the stable form of carbon above 500° C., consequently the vapour pressures of carbon vapour above the solid carbon and graphite at, say, 1100° C. will not be the same, the carbon possessing the higher vapour pressure. In the presence of graphite at 1100° C. carbon will thus gradually sublime and be redeposited in the form of graphite.

Fitzgerald and Forssell have attempted to measure the relative vapour pressures of carbon and graphite at low temperatures between 500° and 700° C. by studying the equilibrium composition $C+CO_2 \rightleftarrows 2CO$, when carbon or graphite in the solid state is present. They found that at 500° C. the vapour pressure of carbon was 3·7 times that of graphite, and at 640° C. 5·4 times as great.

At Niagara, anthracite is used as the carbon for conversion into graphite. The furnace consists of a long trough holding about 6 tons of anthracite mixed with 3 per cent. of oxide of iron, and is finely crushed to the size of rice grains. The anthracite surrounds a carbon electrode core which carries the heating current. Each furnace is about 30 feet long and 2 feet 6 inches wide and deep, constructed of fireclay bricks with a carborundum slab liner. The terminal plates at each end of the furnace are water-cooled, since they have to carry over 15,000 amperes.

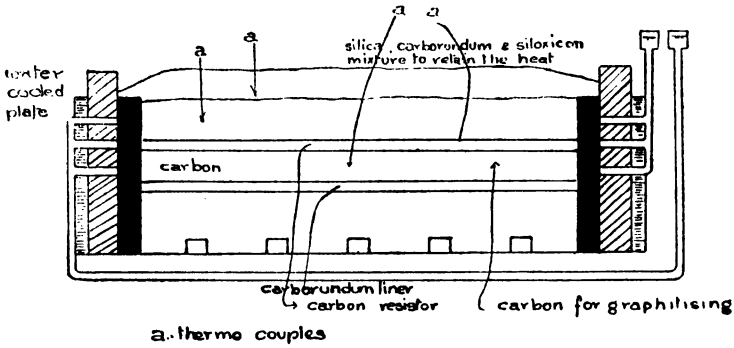

FIG. 17.—Resistance Furnace for the production of Graphite.

About 1600 kw. are consumed per furnace, commencing at 8000 amperes at 200 volts, and as the resistance decreases with elevation of the temperature the current at the end of the operation is about 20,000 amperes at 0·80 volt. The furnace takes about a day to heat up, and from four to five days to cool down. The resulting graphite is remarkably pure, usually containing only from 0·1 to 0·8 per cent. mineral ash, chiefly iron which has not been completely removed by volatilization.

The adequate protection of the pyrometer couples embedded in the anthracite is a matter of considerable difficulty. The limits of the graphitizing zone, which is well over 2000° C., have to be continuously observed so as to ensure the presence of a non-graphitic colder anthracite liner between the graphite and the fusible firebrick.

Small traces of sulphurous gases are liberated as well as carbon monoxide and dioxide during the primary heating up, which in time destroy metal pyrometer sheaths and penetrate all materials such as fireclay and alundum; a new form of very dense alundum, recently introduced, has proved the most satisfactory material.

Acheson[48] has more recently introduced a soft form of graphite for lubricating purposes. Soft graphite can be prepared by raising the silica content of the anthracite to 65 parts of coal with 35 parts of sand. The mixture surrounding the carbon-starting resistor is itself surrounded by a mixture of carbon and sand having a still higher resistance (1 part of coal to 2 parts of sand).

Soft graphite mixed with grease, oil or water is on the market as lubricants under the names of Gredag, Oildag, and Aquadag respectively.

For the preparation of electrodes, petroleum coke is crushed and calcined to expel the volatile matter, then ground in a pulverizer and mixed with pitch with a limited quantity of petroleum, in steam-jacketed kettles. The plastic material is pressed hot into the shape required, usually under considerable pressures, cut into lengths, covered with sand, and baked in a gas-fired furnace. When graphite carbons are required 3 per cent. of oxide of iron is added to the original coke; the carbons are built up in the graphitizing furnace arranged transversely to the current-flow and packed in granulated coke for treatment. The addition of small quantities of ammonia and gallotannic acid is said to improve the nature of the product.

The energy consumption per kilogram of anthracite converted into graphite can be calculated as follows:[49] Taking the mean specific heat of graphite between 20° C. and 2200° C. as 0·45, the energy required to heat up 1 kilogram of graphite will be 990 calories (0·45 × 2200). The heat evolved during transformation of the carbon into graphite is 236 calories per kgm., hence the total heat required is 990 − 236 = 754 cals. or 0·88 kw. hour per kgm. In actual practice from 3 to 3·3 kw. hours are required per kgm.

Processes of electrical graphitization have been applied to various grades of coals, and even to dried peat, but have not proved technically successful.

PHOSPHORUS.

Phosphorus is being produced in increasing quantities by electrothermal methods. The process consists essentially of smelting a mixture of bone ash or the minerals apatite, wavelite, and rock phosphates with carbon and silica to obtain a liquid calcium or aluminium silicate slag and phosphorus vapour diluted with carbon monoxide, according to the equations—

$$Ca_3(PO_4)_2+3SiO_2+5C=3CaSiO_3+5CO+2P$$
$$2AlPO_4+3SiO_2+3C=Al_2(SiO_3)_3+5CO+2P$$

The chief difficulties associated with the electrical production of phosphorus are those associated with its condensation and the ease with which the phosphorus vapour will penetrate through porous materials, even through the furnace walls.

The first satisfactory furnaces, designed by Readman and Parker, were operated on the resistance system, the electrodes being disposed horizontally near the base in a firebrick cylinder with a domed roof. The charge is continuously fed in through the roof by means of a screw conveyer so as to exclude air, and the slag is drawn off by intermittent tapping every three or four hours. Reduction is said to commence at 1150° C.[50] and to be completed at 1460° C. The phosphorus is condensed in copper vessels under water.

With ores containing but small quantities of iron, 80–90 per cent. recovery is obtained in this kind of furnace.

In later designs of furnace, such as those of Irvine, Machalske (Anglo-American Chemical Co.) and Landis (American Phosphorus Co.), certain improvements have been incorporated, *e.g.* phosphorus and slag resisting furnace liners made of vitrified brick set in an asbestos sodium silicate mortar. Horizontal carbon electrodes have been eliminated, and either one or more pendent electrodes substituted. The furnaces operate either on the arc or resistance system, more frequently the former, the arc being formed either between the electrodes themselves or between the electrodes and an annular carbon ring set in the furnace walls.

The earlier pattern furnaces had an output capacity of 80 kgm. of phosphorus per day; the later ones are said to be capable of producing the same amount in one hour.

According to S. Richards [51] the energy consumption for the smaller furnaces was about 11·5 kw. hours per kgm. phosphorus. In more modern and larger units this has been reduced to 5 kw. hours per kgm.

ARSENIC.

The electrothermal production of arsenic is being developed by the Arsenical Ore Reduction Co., applying the Westman process to the ore deposits in Ontario.

The ore consists chiefly of mispickel, $FeS_2.FeAs_2$, a thioarsenide of iron. On heating in a reducing atmosphere a matte of ferrous sulphide is obtained containing any gold or silver present in the ore. The arsenic is volatilized and is condensed on the colder parts of the furnace.

In Westman's process the ore is heated by alternating current between cast-iron electrodes in a furnace capable of dealing with 90 kgm. of ore per hour. The ferrous sulphide matte is tapped off from time to time whilst the arsenic is removed from the furnace by a current of nitrogen gas. The furnace space and a set of condensers forms a closed system with a gas blower; at the commencement of a run air is circulated round the system and the oxygen removed by combustion of some of the arsenic in the furnace. During the period of volatilization of the arsenic, condensation in the external condensers takes place.

According to Hering, a metric ton of ore requires some 1000 kw. hours for treatment.

CARBON DISULPHIDE.

All the carbon disulphide used in the various industries in the United States, exceeding 2000 tons per year, is produced in E. Taylor's resistance furnaces at Penn. Yann., N.Y. The electrical preparation of the sulphide is a great advance over the ordinary thermal method, both as regards cost of production, purity and absence of danger to the workmen. The furnace (p. 161) consists of a double-walled cylinder containing packed carbon at the base which serves as a resistor. Dense carbon is not appreciably attacked by sulphur vapour. Fresh carbon is fed in at the base from time to time through the hoppers A, A, of which there are four. Raw sulphur can be fed in through four similar hoppers at the top of the column, B, B, and runs down the annular space between the double walls of the column. By this means it arrives at the reaction chamber at the same temperature at which the carbon disulphide is formed, and serves as a heat interchanger to cool the liberated vapours. The furnaces are each 41 feet high, 16 feet in diameter, and built of iron, and they require a current of 4000 amperes at 40 to 60 volts, transmitted through four electrodes, D, D, each 25 sq. dcm. in cross-section and 1·2 metres long, at right angles to one another, and situate in the base of the furnace. Still larger furnaces are stated to be contemplated.

The molten sulphur (m.p. 115° C.) flows to the base of the furnace, where it slowly vaporizes (b.p. 444·5° C.), passing up through the heated carbon which is maintained at from 800–1000° C. to a layer of charcoal in the tower. The formation of carbon disulphide according to the equation

$$C+S_2=CS_2$$

is complete at a bright red heat.

Charcoal containing less than 3 per cent. ash is used, being fed in through the hopper F situated at the top of the furnace.

Each furnace will yield approximately 1000 metric tons of CS_2 before it is necessary to dismantle and clean out the ash. The output from each furnace is about 7500 kgm.

per day, representing an output of about 1·2 kgm. CS_2 per kw. hour. If we assume that the gases leave the furnace at 200° C., we can calculate the theoretical energy consumption necessary from the following data. The heat of formation—

$$C+2S=CS_2$$

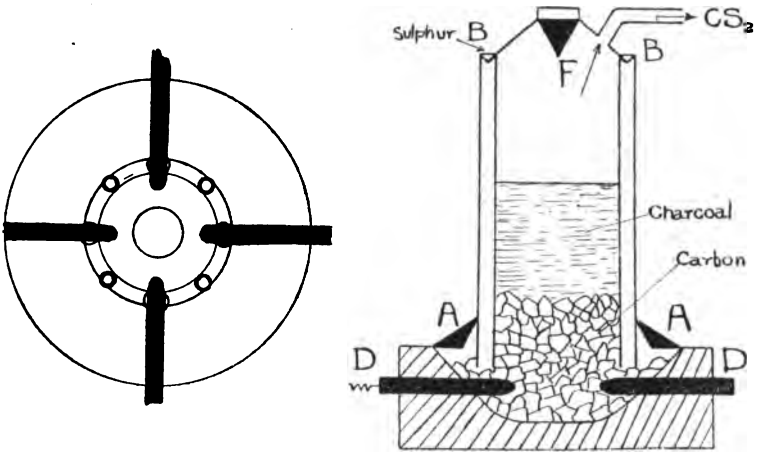

FIG. 18.—Carbon disulphide furnace. Penn. Yann., N.Y.

is 19,000 calories. To vaporize the CS_2 72 calories are required per kgm., and to heat the vapour up to 200° C. we need $200 \times 0{\cdot}24=48$ calories per kgm. The total amount of energy necessary is therefore $250+72+48=370$ calories, equal to 0·45 kw. hour per kgm. or 2·2 kgm. per kw. hour. The furnace thus shows an energy efficiency of 55 per cent.

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SECTION V.—CARBORUNDUM AND THE OXYSILICIDES OF CARBON

THE reactions occurring between carbon and silica at the high temperatures of the electric furnace are very varied, and have led to the commercial production of many industrially important compounds. The chief of these is silicon carbide, named "carborundum" by E. Acheson, the discoverer of the compound in 1891, who at the time was under the impression that the material contained crystalline alumina (corundum).

Carborundum is used in large quantities as an abrasive, as bits for rock drills and the multitude of other uses that a crystalline substance as hard as diamond can be put to. Among the other important uses of the substance may be mentioned its application as a deoxidant in the preparation of steel and as an infusible liner for coal and coke fired furnaces.

Carborundum is prepared in a resistance furnace following the general construction adopted by E. Acheson for the production of graphite (see p. 156). Each furnace is about 10 metres long, 5 metres high and 3 metres broad, built up of brickwork and containing the usual carbon core, about 1 metre in diameter, of ⅜-inch crushed coke. A charge consisting of an intimate mixture of the following composition:—

Sand	52·2 to 54·4	per cent.
Coke	35·4 to 35·1	„
Sawdust	10·6 to 7·0	„
Salt	1·8 to 3·5	„

is loosely packed round the core.

It will be noted that a slight excess of coke is used above the proportions corresponding to the equation—

$$SiO_2+3C=SiC+2CO$$

The function of the salt is to remove the impurities in the coke and sand such as iron by the formation of volatile chlorides. By the addition of sawdust the porosity of the charge is maintained, thus allowing the carbon monoxide formed during the reaction to escape. Each furnace consumes about 2000 kw. At the commencement the resistance is high, necessitating an applied E.M.F. of 200 to 250 volts, falling to 75 volts at the end of the run. During the conversion the carbon monoxide liberated burns between the joints in the brickwork at the sides and the top of the furnace.

The temperature range within which the formation of carborundum is possible is a very limited one, lying between 1550° C. and 2200° C., and it is only by careful control of this factor that successful preparation of carborundum is possible.

On dismantling a carborundum furnace a great variety of products are obtained, formed by the interaction of the constituents.

The exact mechanism by which the various compounds are produced is by no means clear, but their line of demarcation around the core are usually quite well defined. It is found that the carbon core, now completely graphitized, is surrounded by a zone of crystallized carborundum, SiC; then by a layer of carborundum powder; then a ring of siloxicon, "fire sand," Si_2C_2O, mixed with silicon monoxide; and finally a skin of fritted silica.

According to Lampen and Tucker,[1] Gillet,[2] and Saunders,[3] siloxicon commences to be formed at 1500° C. to 1550° C., presumably according to the equations—

$$(1)\quad SiO_2+C\rightarrow SiO+CO$$
$$(2)\quad 2SiO+3C\rightarrow Si_2C_2O+CO$$

whilst at 1820° C. silicon carbide formation commences, being completed at 1920° C. At 2220° C., according to these authors, dissociation of the carbide commences and is completed at 2240° C.—

$$SiC\rightleftarrows Si+C$$

Although the explanation of the production of siloxicon

(Si_2C_2O) from silica and carbon is complete, investigators are not in agreement as to the method of formation of carborundum. It may be produced by the reduction of siloxicon by carbon or silicon at a higher temperature—

$$\begin{array}{ll} (1) & Si_2C_2O+C \rightleftarrows 2SiC+CO \\ (2) & SiO_2+C \rightleftarrows SiO+CO \\ & SiO+C \rightleftarrows Si+CO \\ & Si+Si_2C_2O \rightleftarrows 2SiC+SiO \end{array}$$

or produced by interaction of silicon and carbon vapour, the silicon being formed according to either of the following equations :—

(*a*) From siloxicon, $SiO+C \rightleftarrows Si+CO$
(*b*) From carbide and silica, $SiO_2+2SiC \rightleftarrows 3Si+2CO$

J. Richards[4] has calculated the probable vapour pressure of carbon at various temperatures, with the following results :—

Temperature.	Vapour pressure mm. Hg.
1820° C.	0·001
1920° C.	0·005
1960° C.	0·01
2000° C.	0·02
2060° C.	0·03
2100° C.	0·05
2155° C.	0·10
2215° C.	0·20
2255° C.	0·30

He considers that this small vapour pressure is quite enough to account for the growth of carborundum crystals from the interaction of silicon and carbon in the vapour form. In the presence of an excess of silicon vapour the dissociation of the silicon carbide formed would of course be depressed, thus permitting of slightly higher working temperatures.

Tone[5] believes that the formation of the carbide is brought about by the interaction of carbon monoxide and silicon vapour according to the equation—

$$3Si+2CO \rightleftarrows SiO_2+2SiC$$

By the direct interaction of carbon and silica we can write the equations for the production of silicon carbide and siloxicon as follows :—

$$\text{(1)}\quad SiO_2+3C=SiC+2CO$$
$$\text{(2)}\quad 2SiO_2+5C=Si_2C_2O+3CO$$

In view of the extreme rareness of molecular reactions of such a high order it is extremely probable that the direct formation of these compounds does not take place, but they are the result of a series of simpler reactions such as those outlined above.

With Allmand[6] we may calculate the energy necessary for the production of carborundum as follows :—

The heats of formation of silica, silicon carbide and carbon monoxide are respectively—

$$Si+O_2=SiO_2+180{,}000 \text{ calories.}$$
$$Si+C=SiC+\ 2{,}000 \text{ ,,}$$
$$C+O=CO+\ 29{,}200 \text{ ,,}$$

Hence the production of 1 kilomol (40·3 kgm.) of carborundum at room temperature requires 180,000+2000−(2×29,200)=119,000 calories. We can further assume that the carborundum is heated to 2100° C., whilst the liberated CO on passing through the cold surrounding charge leaves the effective part of the charge at 1400° C. The mean molecular specific heats of carborundum and carbon monoxide between 0° and 2100° C. and 0° and 1400° C. respectively are 11·3 and 7·1.

The heat required can be summarized as follows :—

To forming carborundum =119,600 calories.
To heating up SiC, 11·3×2100 = 23,700 ,,
To heating up CO, 2×7·1×1400 = 19,900 ,,
Total=163,200 ,,

$$=\frac{163{,}200\times 4\cdot 19}{40\cdot 3\times 3600}$$

=4·7 kw. hours per kgm. or 4700 kw. hours per metric ton.

In technical working about 8360 kw. hours per metric ton of carborundum are consumed, and only 50 per cent. of the charge is converted.

The product is manufactured by the Carborundum Co. at Niagara (10,000 kw.), and a smaller plant at Dusseldorf, Germany, is controlled by the same company.

SILUNDUM, SILFRAX.

Owing to the resistant properties of carborundum, the substance being unattacked by oxygen even up to very high temperatures or by acids, attempts have been made to prepare moulded articles of the material in a compact form. It was found that moulded carbon articles could be converted into a semi-metallic state by exposure to silicon vapour ("silidizing"). The resulting product, termed silundum, retains its original shape and possesses all the properties of carborundum. It is electrically conducting and can be used for resistance material for temperatures up to 1200° C.

Carbon articles are packed in a charge of the composition required for the production of carborundum in a heating furnace of the usual resistance type. The carbon is converted into silundum, beginning at the outside and continuing to a depth depending on the period of heating. Fitzgerald has attempted to prepare articles of carborundum by moulding crystallized carborundum into the desired form and subsequently recrystallizing the mass in an electric furnace. Tone adopted "fire sand" or amorphous carborundum to the same purpose, using water glass or glue as a temporary binder.

He[7] also investigated the action of silicon vapour on carbon at various temperatures, and showed that between 1550° and 1820° C. the carbon was converted into amorphous silicon carbide between 1820° and 2220° C. into the crystalline variety. He found evidence of the existence of solid solutions of silicon in silicon carbide when the penetration was most effective, *i.e.* if silica in excess of the quantity required for the preparation of carborundum be added to the charge in which the articles are packed. The modification of silundum produced under these conditions he terms "silfrax." The maximum penetration of silicon vapour into pure carbon is 0·5 inch. "Silit," as prepared by the Siemens Co. in Germany, appears to have been identical with silundum.

MONAX.

Potter,[8] who investigated the various products formed in the carborundum furnace, isolated crude silicon monoxide as a reddish-brown powder, to which he gave the name "monax." It has a limited field of usefulness as a reducing agent, a heat insulator (it has an apparent density of only 0·04), and a polisher of fair abrasive power. It has also been suggested to use it as a pigment and in the preparation of printers' inks.

SILOXICON AND FIBROX.

We have already referred to the preparation of siloxicon or silicon oxycarbide in one of the outer zones of the carborundum furnace. The oxycarbides of silicon were first isolated by Cohen in 1881,[9] who obtained various different compounds on heating silicon in a stream of carbon dioxide. In 1903, Acheson [10] developed the preparation of "siloxicon" for technical purposes, and not merely as a by-product in the manufacture of carborundum.

"Siloxicon" apparently includes a series of compounds of the general formula Si_xC_xO, where x lies between 1 and 7, and averaging 2 when large samples are taken. It is an amorphous powder highly refractory and indifferent to most acids; forms a suitable lining to furnace walls, but is more easily oxidized than carborundum, a superficial silica glaze being produced according to the equation—

$$2Si_2C_2O+7O_2=2SiO_2+4CO_2$$

It can be moulded and baked to form vessels of various shapes. At high temperatures in an inert atmosphere it decomposes into carbide and silicon as follows :—

$$Si_2C_2O=SiC+Si+CO$$

Tone has expressed the view that siloxicon may consist essentially of a solid solution of silica in silicon carbide, since on treatment with hydrofluoric acid it is freed from silica and silicon, and a residue of amorphous silicon carbide remains behind.

Acheson's method of preparation is carried out at the International Graphite Co.'s works at Niagara. A carborundum furnace is used, although occasionally modified by the introduction of multiple carbon cores instead of a single one. The charge consists of a one-third coke and two-thirds silica with the usual admixture of a little sawdust and salt. As has already been noted, the formation of siloxicons occurs at a lower temperature than that necessary for carborundum.

Both F. Tone and E. Weintraub have succeeded in preparing an interesting modification of siloxicon. The material termed "Fibrox" by Weintraub consists of fine threads of siloxicon (0·3 to 0·6μ diameter), frequently several inches long. It serves as a remarkably efficient heat insulator owing to the fineness of the fibres; at the same time, in common with carborundum, it is a good electrical conductor. Its apparent density is said to lie between 0·0025 and 0·0030 (2½ to 3 gms. per litre). It can be formed by allowing carbon monoxide slowly to diffuse into a vessel containing silicon vapour at a temperature just below that required for the formation of carborundum.

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SECTION VI.—THE CARBIDES AND BORIDES

OUR knowledge of these products of the electrical furnace is due chiefly to the work of Moissan, who isolated the first carbide, that of calcium in a pure state, in December, 1892, by reduction of lime with carbon. The carbides as prepared in the electric furnace are all dark metallic-looking solids with a crystalline fracture. Most of them react with water to give off hydrocarbons with reformation of the oxide, *e.g.*—

$$CaC_2+2H_2O=Ca(OH)_2+C_2H_2.$$

The products of decomposition are shown in the following list:—

Carbide.	Product.
Fe_3C	No action with water.
Cr_4C and Cr_3C_2	
Mo_2C	
W_2C	
SiC	
TiC	
Cs_2C_2	C_2H_2
Na_2C_2	
K_2C_2	
Rb_2C_2	
Li_2C_2	
CaC_2	
SrC_2	
Ba ~~Ca~~C_2	
BC_2	CH_4
Al_4C_5	
Mn_3C	CH_4 and H_2
CeC_2	CH_4, H_2, C_2H_2 and traces of other volatile hydrocarbons.
LaC_2	
PrC_2	
NiC_2	
SnC_2	
YC_2	
ThC_2	
U_2C_2	Volatile and liquid hydrocarbons.

The carbides most important industrially are those of calcium and silicon, the former being used for the production of acetylene and as an intermediary in the cyanamide industry as well as a reducing agent in electrothermal work, the other, the preparation of which has already been discussed, as an abrasive and in small quantities as a reducing agent.

Calcium Carbide.

Calcium carbide is produced in electric arc furnaces according to the following reaction :—

$$(1)\ CaO + 3C \rightleftarrows CaC_2 + CO$$

The reaction is reversible, and elevation of the temperature shifts the equilibrium over in favour of the formation of the carbide. Simultaneously with this reaction other side reactions take place in the furnace, viz. the formation of calcium from the oxide and the carbide according to the equations—

$$(2)\ CaO + C \rightleftarrows Ca + CO$$

$$(3)\ CaC_2 \rightleftarrows Ca + 2C$$

and the dissociation of the carbon monoxide—

$$2CO \rightleftarrows 2C + O_2$$

Several attempts have been made to determine the pressure of CO required for equilibrium at various temperatures.

According to Allmand [1] the measurements of Rudolphi [2] and Thompson [3] are most correct; the mean values found were—

Temperature.	P.CO in mm. Hg.
1575° C.	5·0
1675° C.	25·3
1775° C.	107·0
1875° C.	405·0
1975° C.	1330·0

The reaction between lime and carbon begins at about 1500° C., and fusion of the carbide commences at 1800° C.,[4] but in actual practice the resulting carbide is nearly always heated to 2000° C.[5] At this temperature a pressure of nearly two atmospheres of CO would be necessary to reconvert the carbide back into lime and carbon. If the temperature be raised too high the carbide is said to be "burnt," dissociation of the carbide into graphite and calcium vapour taking place according to reaction (3), the resulting calcium acting with the carbon monoxide present to reform lime and carbon dust, which are carried off in the gas stream.

There have been several calculations made on the theoretical energy expenditure necessary for the production of one metric ton of pure calcium carbide from lime and carbon, varying from 1523 kw. hours to 3837 kw. hours (Gin). Several investigators have given no details as to the temperature at which the various products (CO and CaC_2) are supposed to leave the furnace, and there is still some uncertainty in the values of the specific heats of lime and carbon at high temperatures, as well as the heat of formation of calcium carbide.

We will adopt the following values as the basis of calculations :—

Atomic specific heat of carbon $= 4{\cdot}26 + 0{\cdot}0072T$
Molecular specific heat of lime $= 11{\cdot}4 + 0{\cdot}001T$

$$\left.\begin{array}{llll} \text{Heat of formation of} & CaO & = 145{,}000 & \text{calories} \\ \text{,,} \qquad \text{,,} & CO & = 29{,}200 & \text{,,} \\ \text{,,} \qquad \text{,,} & CaC_2 & = 3{,}900 & \text{,,} \end{array}\right\} \text{per gram molecule}$$

If we assume that the carbide and carbon monoxide leave the furnace at 2000° C., and are not used to heat up the incoming charge, we may calculate the energy required as follows :—

$$\begin{array}{c}\text{Heat}\\ \text{supplied to}\end{array} \left\{\begin{array}{ll} \text{raise 1 mol CaO from } 0^\circ \text{ to } 2000^\circ \text{ C} = & 24{,}800 \\ \text{decompose 1 mol. CaO into Ca and } O_2 = & 145{,}000 \\ \text{raise 3 mols of C from } 0^\circ \text{ to } 2000^\circ \text{ C.} = & \underline{30{,}000} \\ & 199{,}800 \end{array}\right.$$

$$\begin{array}{c}\text{Heat liberated}\\ \text{by formation}\end{array} \left\{\begin{array}{ll} \text{of 1 mol CO} = & 29{,}200 \\ \text{of 1 mol } CaC_2 = & \underline{3{,}900} \\ & 33{,}100 \end{array}\right.$$

Net energy required = 166,700 calories or
= 3,040 kw. hours per metric ton,

a figure closely approximating to that which Haber obtained (3100 kw. hours) by a somewhat different method, in which he assumed that the value of Q in the reaction—

$$CaO+3C+Q=CaC_2+CO$$

was equal to 121,000—3·3T, a value determined by Thompson (*loc. cit.*). Commercial calcium carbide averages 85 per cent. purity, and the energy consumption per ton of 85 per cent. carbide varies between 3500 and 5960 kw. hours, depending on the construction of the furnace and the system of operation.

The carbide furnace was originally designed for heating by means of an electric arc, but, as in most other electrothermal processes, the tendency to make use of "resistance" heating has led to very considerable modifications of the types of furnace employed and incidentally to an increased thermal efficiency. It is, however, doubtful whether any carbide furnace operates purely on the resistance principle, since owing to the presence of both calcium and carbon vapour in the hot charge, the E.M.F. necessary for striking an arc can be reduced to 8 volts. It appears more probable that the best furnaces act as smothered arc furnaces, in which small arcs are continually made and broken by the movements of the charge. Both alternating and direct currents have been used; the most uniform product is obtained with the former, but in badly designed furnaces there is frequently a considerable loss of energy due to self-induction.

The charge consists of a mixture of carbon and crushed limestone in the theoretical proportions. If no loss were maintained 1440 kgm. of the charge should produce 1000 kgm. of carbide; in practice from 1700 to 3000 kgm. of charge have been found necessary for this output. The two important factors in the charge which influence the yield and the energy consumption are: (1) Size and uniformity of composition, and (2) Presence of impurities. It has been found that a finely comminuted charge is inadvisable. The evolution of carbon monoxide during the process of formation of the carbide causes honeycomb channels to be formed in the interior of the mass, frequently glazed on their interior surfaces; this results in the loss of a considerable amount of heat due to the ease with which the hot gas can escape from the charge without heating it. When the channels become numerous a mass of overlying charge may subside, causing a large fluctuation in the furnace load and at the same time liberating a sudden burst of gas which carries with it a portion of the finely powdered charge. In practice the most uniform results are obtained by using lime crushed to 1 inch and the coal to $\frac{1}{8}$-inch or $\frac{3}{16}$ inch.

The lime for carbide manufacture should be thoroughly burnt and free from moisture. The carbon in the form of coke, anthracite, or charcoal should have as low an ash content as possible. Coke containing more than 10 per cent. ash can only be used with great difficulty, and less than 5 per cent. ash is desirable. Anthracites containing 3 per cent. ash, or less, are usually employed. Small quantities of carbonized wood and sawdust, the by-product of wood distillation, find their way into the carbide industry and give the best results.

The usual impurities are magnesia and alumina, which assist in the formation of thick crusts in small furnaces and cause the molten carbide in the larger furnaces to become viscous and not so easily tapped; small quantities of arsenic, phosphorus and sulphur present in the coal or in the lime as calcium phosphate or sulphate are reduced to phosphides, arsenides and sulphides in the furnace.

When treated with water impure carbide will liberate phosphine, arsine and hydrogen sulphide, all objectionable on account of their toxic properties. In addition, impure phosphine is spontaneously inflammable. The other coal ash constituents, silica, oxide of iron and the alkalis, do not sensibly affect the operation of the furnace.

Various alternative schemes have been proposed to ensure the preparation of pure carbide from impure materials so as not to limit the manufacturer to the purchase of pure anthracite and lime. Rathenau suggested the addition of iron to the melt to remove the silica as ferrosilicon, which may be drawn off from the bottom of the furnace below the carbide. Hewes adds a quantity of limestone and about 2 per cent. of manganese dioxide to the charge. The carbon dioxide liberated from the carbonate serves to carry impurities such as the calcium sulphides and phosphides to the surface crust, whilst the manganese carbide formed lowers the melting point of the calcium carbide, permitting it to be easily tapped.

The addition of crude hydrocarbon oil to the lime instead of heating up a mixture of carbon and lime is said [6] to give a loose non-coherent, non-hygroscopic carbide.

Calcium carbide furnaces of three distinct types are in use at the present time—

(1) The " block " or " ingot " type.
(2) Tapping furnaces.
(3) Continuous furnaces.

(1) **Ingot Furnaces.**—The earlier forms of carbide furnaces were all of the " ingot " type, such as the Willson, Bullier and Horry furnaces. In these furnaces a charge of lime and coke is fed in, and when a sufficient amount of carbide is formed the furnace is removed and allowed to cool. The contents are then broken up and the fused carbide separated from the half-formed and non-converted material; the latter is returned to the furnace with the next charge. The earlier Willson furnace (Fig. 19, A) had one basal and one pendent electrode which was continually raised as the block of molten carbide increased in size. Owing to the loss of energy occasioned by transmission of the current through the partly solidified mass, the improved Willson (Fig. 19, B) was introduced having two pendent electrodes.

As has already been observed, only part of the charge is converted, the unconverted and semi-fused materials acting as a protecting liner for the iron furnace walls. Several of such furnaces are generally run together, each taking a charge of about 1400 kgm. and an energy consumption of 200 to 250 kw. at 50 to 70 volts. About

800 kgm. of carbide is formed from this charge after a 13-hour run. The energy consumption of 6000 kw. hours per metric ton of 85 per cent. carbide has been reduced to 4500 kw. hours in the later designs of the Willson furnace, but the labour cost of breaking up and sorting the ingot is always high.

In the Horry furnace of the Union Carbide Co., Niagara (Fig. 19, C), a successful attempt has been made to apply the ingot system to a semi-continuous operation. A wide horizontal spindle carries two rings about 2·5 metres in diameter and 1 metre apart. By means of movable plates the space between the plates can be converted into a chamber of rectangular cross-section in which the reduction of the carbide takes place. Two electrodes are mounted in a hopper supplying the charge at one point in the ring, the outside plates being then removed for the purpose. The spindle is slowly rotated so as to remove the molten carbide from the base of the hopper as rapidly as it is formed, thus allowing a fresh charge to accumulate above the old one.

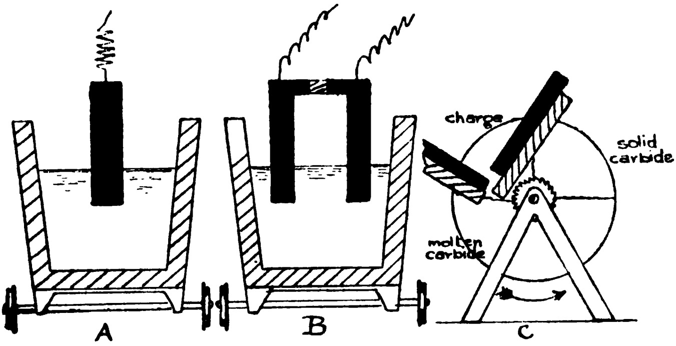

FIG. 19.—Calcium carbide furnaces. "Ingot" type.

After a complete rotation the cover plates are removed and the ring of solidified carbide broken up. A complete revolution is made in 24 hours and about two tons of carbide are produced. With a load of 375 kw. per furnace [7] a production of 1 metric ton per 4500 kw. hours is thus obtained. According to Stansfield,[8] the energy consumption can be brought down to 310 kw. per furnace, thus producing 1 metric ton for 3800 kw. hours.

(2) **Tapping Furnaces.**—With an increase in the furnace size to reduce the radiation heat loss and the labour cost per ton of material, a corresponding increase in the efficiency of working and ease of control of temperature was obtained. The practicability of tapping a large mass of molten carbide impossible in the smaller furnaces owing to the formation of crusts and the high viscosity of the impure melt was investigated in many carbide works.

The Alby Carbide Co. at their Odda works use a furnace very similar to the early Willson pattern provided with tapping holes in the end walls. Each unit will take 1000 kw. at 50 volts and is tapped once every 45 minutes. A considerable economy is effected both in current and in raw material, 1500 kgm. of charge being used to produce 1 metric ton of carbide as against a theoretical charge of 1400 kgm. The energy consumption is stated to vary from 4200 to 4500 kw. hours for 1000 kgm. of carbide.

(3) **Continuous Furnaces.**—Several improvements have been made in tapping furnaces so as to ensure continuity of production, especially by Helfenstein,[9] by Memmo in Italy, and in the Norwegian carbide works. When large open arc furnaces are used a limit is set to the power consumption by the difficulties of working and the nuisance from fumes. The present tendency is to use large multiple-phase current furnaces, which are totally enclosed. By this means the radiation loss from the upper surface of the charge is minimized and the opportunity of collecting the carbon monoxide evolved presents itself.

Helfenstein has used a 9000-kw. 3-phase furnace, furnished with three electrodes, one to each phase, with satisfactory results. The practical limit to the current consumption in an enclosed furnace is set only by the size of the electrodes, which should not carry a current exceeding 500 ampères per sq. dcm.

Borchers suggested water cooling the furnace for the purpose of steam generation with the waste heat; this idea does not seem to have received technical application. The carbon monoxide leaving the furnace at 2000° C. can be utilized for burning the limestone and preheating the entering charge.

The energy liberated in the combustion of one gram-molecule of carbon monoxide is approximately 67,700 calories, whilst the energy required to heat up 3 molecules of carbon and one molecule of CaO in accordance with the equation—

$$CaO+3C=CaC_2+CO$$

from 0° to 2000° C. is, as we have seen, only 54,800 calories.

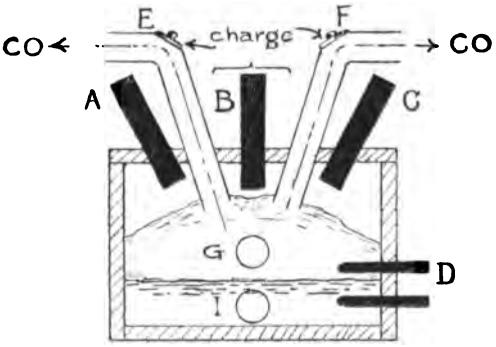

FIG. 20.—Calcium carbide furnace. Three-phase continuous type.

It should, therefore, be possible to heat up the charge to the reaction temperature by the combustion of the carbon monoxide liberated during the formation of the equivalent amount of carbide. By preheating the charge to 2000° C. the consumption of energy required for the production of 1 metric ton of carbide would be reduced to 2100 kw. hours.

The carbon monoxide can, of course, be burnt after parting with its heat to the incoming charge, as indicated in the accompanying diagram. The energy thus derived may be used for raising steam or burning the limestone. In some modern furnaces an auxiliary basal electrode, D, is fitted, through which a current can be supplied during the process of tapping. By this means a high temperature is maintained at the tap hole, and a steady fluid stream of molten carbide is obtained.

Water cooling the electrode holders has further minimized the consumption of electrode material. Sufficient evidence is not yet to hand as to the highest electrical efficiency obtainable with this type of furnace, but individual experimental runs have shown the possibility of producing a metric ton of carbide with an energy consumption of only 3800 to 4000 kw. hours.

The preparation of borides is not accomplished on an industrial scale. In view of the remarkable abrasive powers of certain borides which exceed carborundum and alundum in hardness, an outlet for a small supply of a high-grade material might be found. Their method of preparation is on a small scale similar to that adopted for calcium carbide.

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SECTION VII.—ELECTROTHERMAL NITROGEN FIXATION BY METALS AND METALLIC COMPOUNDS

IN 1898 Sir William Crookes, in his presidential address to the British Association, drew the attention of the scientific world to the growing importance for a satisfactory solution of the nitrogen problem.[1] National and international economic and political existence all centre around the land question, and we find that fixed nitrogen is an essential for the production of food from the land. Approximately four-fifths of the world's supply of nitrogenous materials are used as fertilizers, the remaining one-fifth in the chemical industries, chiefly as cyanides for the extraction of gold, as nitric acid for the production of explosives, and in various forms for the diverse branches of the organic chemistry industry, especially the dyes.

With the natural increase in the density of the population, a corresponding increase in intensive horticulture is necessary, and we find that Belgium, one of the most densely populated areas of the world, uses more nitrogenous fertilizers per acre than any other country, and a corresponding increased yield per acre of foodstuffs is obtained, whilst in the almost virgin soils of the wheat areas in America, Canada and Siberia the application of any nitrogenous fertilizer has not yet been found necessary. Apart from these natural tendencies towards an increased consumption of artificial fertilizers, the development of certain social factors, such as the system of peasant proprietorship ensuring a greater interest in the land, the increased scientific education of the people leading to a more rational view as to the needs of the soil; and the increased power of purchase by means of guilds and co-operative societies, all indicate that the demand for artificial fertilizers is certain to increase at a greater rate than it has done in the past.

The present sources of supply may be briefly enumerated as follows :[2]—

Nitre.—Large deposits of natural sodium nitrate, "caliche," are found in Chile. These have been worked on an ever-extending scale since 1830, the present output amounting to over two and a half million tons per annum. Although these deposits appeared inexhaustible when first worked, the increasing consumption has led to various carefully investigated surveys of the area to determine the probable available supplies. The reports submitted to the Chilean Government have exhibited a diversity of opinion, and although the somewhat alarming figure of 21 years as the maximum period of life can be rejected, it appears that before the end of the present century the economic exportation of Chilean nitre will no longer be possible.

Less important deposits of nitrates of sodium and potassium are found within the British Commonwealth, namely in India, the Sahara, Egypt and Persia, and will probably be developed locally.

Ammonia.—The other chief source of supply of combined nitrogen is ammonia, which is used in the form of ammonium sulphate. Recently experiments by Rossi and others have indicated that ammonium nitrate can also be used as a fertilizer. It may be remarked that since ammonia can be converted into nitric acid by combustion with air or oxygen on the surface of suitable catalytic material or by oxidation in aqueous solution, the production of a fertilizer from ammonia is not necessarily dependent on the sulphuric acid industry. Practically all the natural ammonia available is recovered from coal distillation either from gasworks or coke ovens. Only about 20 per cent. of the fixed nitrogen in the coal is obtained in the usual distillation process, but a somewhat better recovery is obtained in Mond Gas Producers (60 per cent.), whilst still smaller amounts are recovered from shale distillation and blast furnaces.

The world's annual coal production is over one thousand million tons, of which Great Britain supplies over 15 per cent. Since coal contains on the average 1 per cent. of nitrogen, with a 20-per-cent. recovery two million tons of fixed nitrogen in the form of ammonia would be available if at least partial carbonization of all coal were made compulsory. It is evident that the present available supplies from this source alone could entirely replace the Chilean nitre if the requisite legislation were introduced. Although the world's coal reserve is larger than the Chilean caliche, their period of economical working is by no means indefinite.

Other sources of ammonia are found in the by-products of the destructive distillation of bones and the organic residues in fermentation industries. Probable sources of natural fixed nitrogen will possibly be found in the extended development of the gasification of the low-grade fuels such as peat and turf, of which extensive areas are found within the British Empire, especially in Canada and Ireland; and in the more extensive application of sewage works sludges to manurial purposes.[3] At the present time these potential sources of natural ammonia are not being economically developed; the bulk of the nitrogen in the coal is entirely lost owing to the extravagant methods of fuel combustion employed, whilst the technical difficulties associated with the drying of sewage sludge, peat and turf to render it suitable for fuel have not yet been satisfactorily solved. As a consequence, during the last ten years there has been a considerable development in methods suitable for the technical fixation of atmospheric nitrogen. These may be classified as follows :—

A. The direct preparation of nitric acid by oxidation of the atmospheric nitrogen in the electric arc, and by combustion of gaseous fuel.

B. The preparation of synthetic ammonia from its elements.

C. The fixation of atmospheric nitrogen by biochemical methods.

D. The preparation of combined nitrogen from which ammonia can be obtained, *e.g.* cyanamides, cyanides and nitrides.

A. (1) **The Arc Process.**—The pioneer work connected with this method was accomplished in England by the investigations of Cavendish 1781, Davy 1800, Rayleigh 1897, and McDougall and Howles, who erected the first technical plant in 1899 at Manchester. An outline of the present industrial arc processes, the operation of which is practically confined to Norway, although smaller plants are in operation in Switzerland, Italy, France and Germany, are discussed in another volume of this series. It may, however, be pointed out that the electrical efficiency of the process is very poor, the yields obtained in technical processes being only from 65 to 75 gms. of nitric acid per kw. hour. The efficiency of a normally operating furnace of the Birkeland, Schönherr or Pauling type can be calculated as follows: The energy required to form a gramme-molecule of nitric oxide according to the equation $N_2+O_2=2NO$ is approximately 22,000 calories, and although 13,500 cals. are liberated during the formation of nitrogen dioxide according to the reaction $2NO+O_2=2NO_2$, this heat evolution occurring during the last stages of cooling the gases and absorption in water is not technically available as recoverable energy. Since 22,000 cals. are equivalent to 0·0256 kw. hour, this amount of electrical energy must be supplied to form 30 gms. of nitric oxide or 63 gms. of nitric acid. Taking the mean of Nernst, Jellinek and Haber's figures for the equilibrium concentrations of nitric oxide in ordinary air at high temperatures, the mean absolute temperature of the air passing through the arc to give a 2 per cent. NO concentration must be in the neighbourhood of 2500° C. It must, however, be remembered that since equilibrium is obtained with great rapidity at these high temperatures a considerable higher mean gas temperature may be attained in practice, and that the low percentages of gas actually obtained are due to the impossibility of cooling the gases sufficiently quickly to relatively low temperatures. At low temperatures the apparent stability of a gas rich in NO is assured owing to the slowness with which the reverse reaction $2NO = N_2 + O_2$ proceeds. Assuming that a 2 per cent. concentration of NO represents the true value of the equilibrium concentration at 2500° C., the energy necessary to heat up 14 gms. of nitrogen and 16 gms. of oxygen to this temperature is approximately $2500 \times 2 \times \frac{(6 \cdot 8 + 0 \cdot 0006 \times 2500)}{2}$ or 20,600 calories. The total irrecoverable energy consumption is therefore 42,600 calories, or 0·050 kw. hours for the production of 63 gms. of nitric acid, representing an electrical efficiency of only $\frac{0 \cdot 050}{1}$ or 5 per cent. for a technical production of 63 gms. of nitric acid per kw. hour.

The remaining 95 per cent. of the electrical energy passes out with the unchanged air. Partial recovery of this loss is effected by passage of the arc gas through Babcock and Willcox boilers for raising steam. Although no data are available as the amount of energy so recovered, there can be no doubt that the process is extremely wasteful in power. Its chief merits are extreme simplicity and uniformity of action. The erection costs are high owing to the large volume of gas that has to be heated, cooled and passed through absorption towers.

The work of Haber and Koening on chilled arcs, of Rossi on the use of arc furnaces worked under reduced pressure, and more recently of Lowry and Strutt on the production of an allotropic active modification of atmospheric nitrogen, indicate that arc methods may be capable of modification and improvement, possibly departing from the original electrothermal process to an electronic one so as to render it suitable for those countries where the cost of electrical power is the governing factor in electrochemical development.

(2) **By the Combustion of Gaseous Fuel.**—Chiefly owing to the work of Haber and his pupils on the production of oxides of nitrogen during the process of gaseous explosion and combustion, a number of patents have been

taken out for utilizing gaseous fuel for the direct formation of oxides of nitrogen. The only one which has been developed on a semi-technical scale is that of Hausser, in which a mixture of coke oven gas and air or oxygen is exploded in a bomb of large capacity. Provision is made for a rapid cooling of the gases by water injection and rapid release into the cooling system. The process of charging, release, ignition and scavenging, can be made cyclic on a modified Otto cycle.

The mean explosion temperature of 2100° C. when operating with rich coke oven gas should yield an NO concentration in the resulting gases of only 0·5 per cent. or about 5·56 gms. per kw. hour. The inventor has put forth claims to obtaining over 5 per cent. of NO, due to the induced photochemical action favouring the formation of endothermic compounds during the period of explosion. These claims, however, remain to be substantiated.

B. **The Haber Process.**—The successful technical development of the experiments of Regnault and Ramsay on the synthesis of ammonia from the elements nitrogen and hydrogen was made by Haber and the Badische Anilin u. Soda Fabrik at Oppau and Leverkusen in Germany a few years previous to the outbreak of war. Haber first determined the amount of ammonia in the equilibrium mixture $3H_2+N_2\rightleftarrows 2NH_3$, under high gas pressures and at various temperatures. It will be noticed that from the equilibrium constant equation—

$$K=\frac{C^3_{H_2}.C_{N_2}}{C^2_{NH_3}}$$

increase of pressure increases the equilibrium amount of ammonia present, and furthermore an excess of hydrogen over the stoichometric ratio $H_2 : N_2 : : 3 : 1$ is likewise beneficial for high concentrations of ammonia.

From the general equation—

$$\log\frac{K_1}{K_2}=\frac{Q}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

the dependence of K, the equilibrium constant, on the temperature can be determined provided the heat of formation of ammonia be known. Haber obtained the following concentrations in close agreement with the calculated values, under a pressure of 200 atmospheres in an equilibrium mixture of the three gases :—

Temperature.	Percentage NH_3.
350°	11·7
750°	2·99
950°	1·07

At low temperatures the velocity of conversion is slow, whilst at high temperatures the equilibrium amount of ammonia formed is reduced. The two chief obstacles overcome by Haber were the construction of suitable furnaces to withstand high pressures and the preparation of a catalyst which would bring about the combination of the two gases at low temperatures. Suitable catalysts working extremely actively at very low temperatures 400° to 500° C. were found in osmium and uranium carbide, but difficulties were encountered when technically prepared gases were employed owing to the poisoning of the catalyst by the small traces of impurities such as carbon monoxide, sulphur compounds, oxygen, and the like in the gases. Catalysts more robust but less active were found in electrolytic iron and certain ferrugineous mixtures, such as iron and molybdenum, iron and tungsten, iron and cobalt, ferrocyanides and specially prepared sodamide metal mixtures.

The general arrangements of the Badische plant are fairly well known, but details as regards construction and catalytic material employed are carefully guarded national secrets. The hydrogen is prepared by the "Bamag" process, in which water-gas and steam is passed over a specially prepared iron catalyst at 550° C., when the following reaction proceeds to equilibrium :—

$$H_2+CO+H_2O \rightleftarrows 2H_2+CO_2$$

The equilibrium amount of CO remaining in the gas at this temperature, calculated from the equilibrium constant $K=\frac{C_{CO_2}.C_{H_2}}{C_{CO}.C_{H_2O}}$ is about 2 per cent. The excess steam is removed by condensation, the CO_2 and any sulphur now present as H_2S by pressure washing with water, and the CO is converted to formate by scrubbing with hot caustic soda under pressure. Small traces of the monoxide are removed by a cuprous ammonium carbonate scrubber. The nitrogen is prepared from liquid air or alternatively by so adjusting the air and the steam blasts in the water-gas producer to prepare a nitrogen-hydrogen mixture in one operation. The purified gases are now compressed and passed over palladium asbestos and calcium chloride to ensure the absence of traces of oxygen and water-vapour.

The catalyst "bombs" were originally heated externally, but owing to the weakening of the metal by the combined action of the hydrogen and the high temperature, internal electrical heating is now applied. The gas circulates through the bomb, which contains the catalyst and a system of heat interchange coils. Since the reaction $N_2+3H_3 \rightarrow 3NH_3$ is exothermic, local over-heating of the catalyst may occur, when the amount of heat generated automatically falls owing to decomposition of ammonia already present. The electrical energy necessary for maintaining the catalyst temperature is small when a good system of heat interchange is installed. The ammonia formed in the gaseous mixture is subsequently removed by liquefaction or counter current washing with water under pressure, and the unused gas, augmented by an additional supply from the compressor, dried and recirculated through the bomb. Periodic "blowing off" is necessary to eliminate inert gases such as methane from the hydrogen, and argon present in the nitrogen. The velocity of circulation of the gases is important for the economic production of ammonia. At very low speed equilibrium is obtained, but the yield per litre of catalyst space is small owing to the low velocity of the gas-flow. At very high speeds equilibrium is not obtained, and only a low percentage of ammonia is formed, but the yield per hour is higher owing to the increased velocity of the gas-flow. The space time yield, *i.e.* the yield in kilogrammes of ammonia per litre of catalyst per hour, is the determining factor as far as output of a unit is concerned. In technical operation the space time yield may rise as high as 15. Naturally with increased velocity of gas-flow, the difficulties of heat regeneration and gas circulation are greatly enhanced. The cost of the process is chiefly determined by the expense entailed in the preparation and purification of the hydrogen, the compression of the gases and the skilled supervision necessary.

(C) **Biochemical Nitrogen Fixation.**—In ordinary soil a vast number of bacteria are present, frequently rising to more than 10 million per gramme. These include amongst the several varieties of saprophytic bacteria both ærobic and anærobic, pathogenic organisms and moulds, a number of organisms capable of fixing atmospheric nitrogen, entirely distinct from the nitrifying bacteria of Winogradsky and the more recently discovered denitrifying organisms which are capable of oxidizing or reducing ammonia, nitrates and nitrites already in the soil as such or as nitrogenous organic substances. The first organism possessing this property of fixing nitrogen was isolated by Benjerink, viz. *Aostridium Pastorianum.* Since this period a large number of organisms have been shown to possess this property, such as the fungus *Aspergillus niger, Penecillium glaucum, Phoma betæ* and others, and among the bacteria *Azotobacter chroococcum* and *agilis*, and *Bacillus radiciola.* The conditions for successful nitrogen fixation in soil are briefly as follows :—

1. Presence of calcium, phosphorus and smaller quantities of sodium and potassium.

2. Large quantities of fixed nitrogen hinder further absorption.

3. The temperature range lies between 10° and 50° C.

4. The earth should be well aerated and not contain less than 15 per cent. of moisture.

Most of the organisms function most successfully when growing in symbiosis with other organisms. The azobacter grow most abundantly with certain algæ whilst Hellriegal showed that the *B. radicicola* was practically only associated with leguminous plants such as peas; in this case the plant and bacillus exhibit alternate parasitism. Of recent years several strains of nitrogen-fixing organisms have been cultivated on artificial media for agricultural purposes, and during the period of the war it has been stated that large quantities of nitrogen-fixing yeasts have been grown in Germany for supplying pigs and other animals with their requisite organic nitrogen. In the inoculation of soils the choice of the bacillus employed should be determined by the nature of the contemplated crop, and the activity of the organism controlled before use, since this deteriorates when grown for several generations in artificial media. A good growth is ensured by the addition of a little bacterial pabulum to the soil, such as grape sugar and peptone. Up to the present time these methods have scarcely proved commercially successful.

D. **Electrothermal Fixation of Nitrogen by Metals and Metallic Compounds.**—Elementary nitrogen has been fixed by purely thermal processes in several forms on an industrial scale. Amongst the more important may be mentioned the nitrides, the cyanides and the cyanamides.

All these compounds can be converted into ammonia by treatment with water or steam under a few atmospheres pressure according to the following equations:—

$$X_3N+3H_2O=NH_3+3XOH$$

$$X_2NNC+3H_2O=X_2CO_3+2NH_3 \text{ (under 6 atmospheres pressure)}$$

$$2X_2NNC+2H_2O=(H_2NNC)_2+2H_2O \text{ in water}$$

$$XCN+2H_2O=XCOOH+NH_3$$

$$XCN+2H_2O=XOH+NH_3+CO \text{ (at 500° C.)}$$

The Nitrides.—The technical fixation of nitrogen has been accomplished by Serpek in the Savoy, and although several difficulties prevented the process from being economically successful, yet the advantages of such a process of nitrogen fixation is so great that a reinvestigation of the problem would probably prove remunerative.

Serpek's early experiments (1906–1907) were devoted to the preparation of aluminium nitride by passing nitrogen over aluminium carbide at a red heat, when according to Caro [4] the following reactions take place :—

$$Al_4C_3 \rightleftarrows 4Al + 3C$$
$$4Al + 2N_2 \rightleftarrows 4AlN$$

The dissociation temperature of the nitride is higher than that of the carbide, and consequently the nitride is actually formed through the intermediary preparation of aluminium. From 1907–1910 Serpek was engaged in the construction of apparatus suitable for carrying out the following reaction on a technical scale :—

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$$

The temperature at which the nitride decomposes relatively quickly is 2120° C., and consequently the reaction must take place below this temperature. Serpek states the absorption of nitrogen commences at 1100° C.; at 1500° C. the absorption is fairly rapid, whilst from 1700° to 1850° C. the reaction is a comparatively violent one. We have already noted that alumina purified by the electrothermal method is not readily soluble in the electrolyte used for the preparation of aluminium. A similar observation was made by Serpek in connection with the formation of nitride. Bauxite is more readily converted to nitride than alumina, and absorption commences at a much lower temperature. Tucker and Read [5] confirmed these results and came to the conclusion that low-temperature fixation, desirable owing to the relative ease with which the nitride is again dissociated, can be brought about by suitable catalysts usually present in French bauxite. Serpek successfully operated two different types of furnace in the Savoy. In the first a rotary kiln was employed having transverse carbon resistors heating a charge of bauxite and coke by radiation. The second type of furnace consisted of a hollow vertical shaft containing an axial carbon resistor. The annular space is charged with a mixture of bauxite and coke, and a current of nitrogen passed through the charge at a temperature of 1600° to 1700° C. The liberated carbon monoxide is burnt to heat up the incoming charge. Pure alumina can be recovered from the nitride by decomposition with superheated steam or weak alkali—

$$AlN+3H_2O=Al(OH)_3+NH_3$$

Attempts to use the alumina after dehydration did not prove successful, probably owing to the absence of suitable catalysts. Although the alumina could of course be economically used in the preparation of aluminium, yet the future development of a technical nitrogen fixation process on these lines is more likely to be successful if a continuous process could be devised so as to render the process independent of the need of a supply of fresh bauxite for each charge. From both Serpek and Tucker's observations, it appears possible that a synthetic catalyst could be prepared presumably containing other oxides, such as iron titanium or chromium, which would permit of the successful utilization of the alumina.

Another possible development of the process in which the alumina is treated as a catalyst for gaseous reactions may be imagined as follows: At a temperature of 1500° C. methane is nearly completely dissociated into carbon and hydrogen according to the reversible equation—

$$CH_4 \rightleftarrows C+2H_2$$

whilst carbon monoxide may be converted into methane by hydrogenation over a nickel catalyst (provided the CO,H_2 mixture contain less than 10 per cent. CO)—

$$CO+3H_2=H_2O+CH_4$$

when comparatively low temperatures are employed, *i.e.* under 380° C. At higher temperatures carbon is deposited according to the equation—

$$CO+H_2 \rightleftarrows C+H_2O$$

Either of these reactions obviously permit of the preparation of carbon in a finely divided form. It would therefore seem possible to alternate a steam blow and a nitrogen carbon blow or a nitrogen, hydrocarbon blow through a shaft containing alumina especially sensitized with suitable catalysts maintained at the requisite temperatures. It has been stated that the presence of hydrogen in the gases facilitates the fixation of nitrogen at low temperatures, and these conditions would be maintained in the above imaginary process. The theoretical power consumption for the Serpek process is small, since the reaction—

$$Al_2O_3+3C+N_2=2AlN+3CO$$

requires only 213,000 calories per kgm. mol or per metric ton of fixed nitrogen calculated as ammonia 7300 kw. hours.

It will be noted that 1·5 mols of carbon monoxide are formed per molecule of the nitride, whilst in the case of calcium carbide manufacture only one mol CO per mol CaC_2 is obtained. The gaseous utilizable energy by combustion of the CO is consequently far greater.

If we assume that a reacting temperature of 1500° C. can be utilized by the choice of specially prepared alumina, the energy necessary to heat up one kilomol of alumina, 3 kilomols of carbon and 1 of nitrogen to the reacting temperature is about 40,000 calories. By the combustion of 1·5 kilomols of carbon monoxide 102,000 calories are obtainable. It follows that theoretically 62,000 cals. are available for the process of nitrogen absorption, reducing the amount of energy to be supplied from 213,000 to 151,000 calories, or per metric ton of fixed nitrogen calculated as ammonia from 7300 kw. hours to 5170 kw. hours.

Various patents have been taken out for the preparation of ammonia from other nitrides besides aluminium, especially magnesium, silicon, boron and titanium. There is no evidence that any of them have passed the experimental laboratory scale, and the principles involved are the same as those used by Serpek which have already been discussed.

The Cyanides.—Since the market value of fixed nitrogen in the form of cyanide is greatly in excess of its actual value as a fertilizer,[6] and that at present the most successful synthetic cyanide process, viz. the Castner, utilizes expensive raw materials, sodium, ammonia and charcoal, according to the equations—

$$2NH_3+2Na=2NaNH_2+H_2$$
$$NaNH_2+C=NaCN+H_2$$

a great number of processes have been proposed for the production of cyanides utilizing atmospheric nitrogen. Up to the present time these processes have not been able to compete with the existing ones in which some form of combined nitrogen is used as a starting-point. It is evident that many difficulties would have to be overcome before a cyanide nitrogen fixation process could be developed not only sufficiently economical in operation to compete with the cyanide processes already extant, but providing a sufficient margin in working costs so as to permit of the cyanide so produced to be sold at fertilizer prices after having been converted into some transportable form of ammoniacal nitrogen. During the last few years when the nitrogen shortage has stimulated research, attention has been redirected to these synthetic cyanide processes, and there are prospects that one of these newer modifications, viz. the sodium cyanide process, developed by Bucher, may finally supplant both the synthetic ammonia and the calcium cyanamide processes. In this section only those methods in which electric heating has been used or suggested will be considered; this will naturally exclude a large number, yet those included will be representative and appear to be those which would be most feasible for application on a technical scale.

Cyanogen and Hydrocyanic Acid.—Berthelot first indicated the formation of hydrocyanic acid by passing electric sparks through a mixture of acetylene and nitrogen. The union of acetylene and nitrogen to form hydrocyanic acid proceeds more smoothly when a diluent such as hydrogen is used.

Gruszkrewicz obtained his best yield with a gas mixture of the following composition :—

5 per cent. C_2H_2
5 per cent. N_2
90 per cent. H_2

Better results were obtained when water gas was employed. A 0·3 per cent. conversion was obtained in an hour with a gas mixture containing

54·5 per cent. CO
25 per cent. N_2
20·5 per cent. H_2

The use of the electric arc for the production of hydrocyanic acid has recently been reinvestigated. Lepinski claims a .19 per cent. conversion by passing a gas of the following composition through an arc :—

70 per cent. N_2
20 per cent. CH_4
10 per cent. H_2

whilst the Neuhausen Aluminium Co. are said to employ a gas of the mixture—

5–10 per cent. CH_4
66–81 per cent. H_2
12–24 per cent. N_2

The reaction proceeds smoothly above 1800° C., but the methane content should not exceed 10 per cent. owing to the formation of large quantities of soot. The hydrocyanic acid appears to be formed when the thermal decomposition of the hydrocarbon occurs—

$$CH_4 = 2H_2 + C$$

This reaction only occurs above 1300° C., whilst the decomposition of the hydrocyanic acid itself also proceeds rapidly at high temperatures. Successful development of these processes similar to those employed in the ordinary oxide of nitrogen arc would seem to be indicated where a rapid chilling of the gases after heating is obtained.

No data are available as to the conversion efficiencies of any of these processes, but it is evident that if a 0·3 per cent. yield obtained by Gruszkrewicz can be converted into a 19 per cent. yield as claimed by Lepinski by simple transition from a spark discharge to a high temperature arc discharge when utilizing crude producer gas or producer gas enriched with some hydrocarbon, a cyclic process of heating, heat interchanging and scrubbing the gases with an alkali would certainly prove worthy of investigation.

The Alkaline Earth Cyanides.—Readmann[7] first suggested the use of electrical heating for the fixation of nitrogen by means of a mixture of alkaline earth oxide or carbonate and carbon. As suitable mixture he suggested the following :—

$BaCO_3$	50 kgm.
Charcoal	10 kgm.

The intimate mixture of these substances is introduced into a coke-lined crucible and is heated to a high temperature by the passage of an electric current introduced by means of carbon electrodes inserted in the sides of the crucible. Deoxygenated air or water gas is passed through the mixture. When the latter is used the denitrified residue may be used as fuel. The absorption was said to proceed smoothly according to the equation—

$$BaO+3C+N_2=Ba(CN)_2+CO$$

Part of the cyanide so formed flows out through a lateral opening situate in the bottom of the crucible and part volatilized with the gases, from which it can be recovered by absorption. The optimum temperature of absorption was 1400° C. The above process was slightly modified by Swan and Kendall, in which titanium, molybdenum, chromium or manganese was previously added to the charcoal alkaline earth mixture before absorption of nitrogen. It is stated that with these catalysts the formation of cyanide will commence at a dull red heat, thus avoiding the high temperatures necessary when no catalyst is present.

Mehner suggested the following ingenious process: Fused barium cyanide is electrolyzed between granulated carbon electrodes in an atmosphere of nitrogen gas. Cyanogen is liberated at the anode and can be absorbed in water or caustic alkali; the barium set free at the cathode reacts at the temperature of the melt with the granulated carbon, preferably charcoal, and the nitrogen to reform barium cyanide, which is thus continuously reformed.

The Alkali Cyanides.—The observations of Mond confirmed the earlier experiments of Possoz and Boissière, who erected the first nitrogen fixation factories in the world at Grenall and Newcastle in 1843, of Newton, Swindel, and Margueritte and Sourdeval, in that both the alkalis and alkaline earths readily reacted with carbon and nitrogen to form cyanides at high temperatures. Barium reacted most easily, and many unsuccessful attempts have been made to modify Readmann's process so as to render it commercially feasible. Amongst the alkalis potassium reacted more easily than sodium, and the formation of potassium cyanide was noticed by Dawes and Clarke in the Clyde blast furnaces as early as 1835 and 1837. Thompson in 1839 first drew attention to the catalytic effect of iron, and the catalytic effects of other metals, such as manganese and chromium, were noted by Margueritte and Sourdeval in 1860, and by Swan and Kendall in 1895. Bucher[8] has recently investigated the process, and claims to obtain rapid absorption of the nitrogen in producer gas at a temperature of 900° C., by briquettes of sodium carbonate, coke and iron as a catalyst. Decomposition of sodium cyanide by means of superheated steam is complete at 600° C., according to the following equations:—

$$Na_2CO_3+4C+N_2=2NaCN+3CO$$
$$NaCN+2H_2O=HCOONa+NH_3$$
$$2NaCN+4H_2O=Na_2CO_3+2NH_3+CO+H_2$$

To heat up 1 kilomol of sodium carbonate, 4 kilomols of carbon and one of nitrogen to 900° C. requires 43,000 Calories; the reaction itself is slightly endothermic, 140 Calories being absorbed, and the energy available from the combustion of 3 kilomols of CO is over 200,000 calories. It is therefore evident that the reaction as a whole can be considered as a strongly exothermic one, and in practice should be capable of continuous production without the supply of any extraneous energy.

The carbon consumption per metric ton of ammonia produced would be equal to 1300 kgms. It will be noted that the working temperatures of the cyanide processes are much lower than those necessary for the formation of nitrides or of the carbides, necessary intermediaries for the preparation of cyanamides.

The Cyanamides.—Frank and Caro, in 1895, investigated the preparation of cyanides through the intermediary formation of the alkaline earth carbides, and were the first to study the conditions favourable to the formation of cyanamides. According to the authors the reaction usually expressed by the equation—

$$CaO+3C+N_2=Ca(CN)_2+CO$$

really takes place in several stages—

$$\begin{array}{rl} 1. & CaO+C\rightleftarrows Ca+CO \\ 2. & Ca+2C\rightleftarrows CaC_2 \\ 3\,(a). & CaC_2+N_2=CaCN_2+C \\ (b). & CaC_2+N_2\rightleftarrows Ca(CN)_2 \end{array}$$

The following conditions were found favourable to the formation of calcium cyanamide :—

(1) The nitrogen should be in excess of the theoretical amount required.

(2) A porous carbide is desirable.

(3) Relatively high temperatures should be employed ; for calcium cyanamide 1100° C. appears to be the optimum.

With the overproduction of calcium carbide which took place at the beginning of the century the possibility of utilizing these observations of Frank and Caro for the fixation of atmospheric nitrogen immediately presented themselves, and at the present time the cyanamide industry is a large one, the annual production being nearly half a million tons exclusive of the increased production of the Central Empires during the period of the war. Leblanc[9] investigated the formation of cyanamides of calcium and barium, and came to the conclusion that the relative amount of cyanamide and cyanide formed were dependent on the degree of dissociation of the carbide—

$$
\begin{aligned}
&1. \quad CaC_2 \rightleftarrows CaC + C \\
&\quad\; CaC + N_2 = CaCN_2 \\
&2. \quad CaC_2 + N_2 \rightleftarrows Ca(CN)_2
\end{aligned}
$$

Absorption was found to commence at 700° C. in the case of both barium and calcium carbide, but the barium product always contained large quantities of cyanide. Polzenius and Carlson carried out a series of experiments on the use of suitable addition agents to facilitate the absorption of nitrogen. The chloride and fluoride of calcium were found to give the best results.

Cyanamide of calcium is now manufactured by two processes, the intermittent and continuous. The continuous process is more economical than the earlier intermittent ones and produces a somewhat higher grade product.

In the intermittent process at work at Odda in Norway the carbide is crushed and ground to a fine powder and packed in small sheet-iron drums, each of 300 to 500 kgms. capacity and more recently of 1 to 2 metric tons capacity. The drums, which are lined with refractory bricks, are heated internally by carbon resistors, each drum taking some 20 ampères at 70 volts. Pure nitrogen, which should not contain more than 0·4 per cent. of oxygen prepared by fractionating liquid air by the Linde or Claude processes or by the passage of air over hot copper, is passed in when the temperature has risen to 800° C., and when absorption commences the current is reduced and finally turned off, the temperature being maintained by the reaction, which is exothermic. The absorption is complete after about 30 hours' passage of the gas, during which period the temperature is maintained at from 800° to 1000° C. In practice it is found that 1 metric ton of cyanamide is produced from 0·78 to 0·80 ton of carbide. The contents of the drums are allowed to cool, and after crushing and packing are placed on the market as "Nitrolim," containing some 15 to 20 per cent. of fixed nitrogen.

The electrical energy expenditure required for heating the carbide is about 0·1 kw. hour per kilogram or 500 kw. hours per metric ton of nitrogen fixed. According to recent estimates, the cost of production of one metric ton of nitrogen by fractionation of liquid air should not exceed 15*s*.

Comparison of Nitrogen Fixation Processes.—The various estimates for comparing the costs of fixing nitrogen by the alternative processes already described really offer no guide to the solution of the fundamental problem of the conservation and most economical utilization of the natural resources of the world. It is evident that if large supplies of nitre existed in some nearly inaccessible region, the cost of that nitre delivered to the consumer would be too great to permit of their economical development. In the modern practice, since manual labour can be almost entirely replaced by mechanical work, the international solution of the problem will be decided by one consideration only, viz. the energetic efficiency of the process taken as a whole, *i.e.* the power and material costs involved in taking nitrogen from the air and fertilizing the soil in the chosen areas with it. The national problem is somewhat different, the choice of a method is not solely determined by the efficiency of the process in terms of the energy required to fix a given amount of nitrogen and the transportation costs to the consumer, but the relative costs of the different forms of energy available for that nation, erection and running costs become the deciding factors. In the various processes alluded to two sources of energy are usually required, viz. electrical and carbon in the form of coke; the relative costs of the energy at the factory in these two forms would be thedeciding factors between two equally efficient processes or alternatively between two different proposed factory sites.

In the following table the approximate consumption of energy and coke required to fix 1 metric ton of nitrogen by the different processes are given :—

Process	Kw. hours per metric ton nitrogen.		Coke kgm. per metric ton N_2.		Other source of energy.
Arc ..	60,000–65,000		Nil		Nil
Haüsser ..	Nil		Nil		Gas, 30,000 cu. m. Cal. value 4300 per cu. m. = 150,000 kw. hrs. or 100,000 kgm. coal.
Haber ..	For gas compression ..	1,200	For prep. of H_2		
	For N_2 preparation ..	700			
	For heating catalyst ..	600	Water gas production	2,400	
	For circulation of gases ..	200	"Bamag" H_2 production	1,600	
		2,700		4,000 kgm.	
Serpek ..	For N_2 preparation ..	700	1,300		
	For reduction and azotising	9,000			
		9,700			
Bucher ..	For N_2 preparation ..	700	1,710		
Cyanamide	For production of the carbide	15,000	1,400		
	For azotizing ..	500			
	For grinding ..	700			
	For production of the nitrogen	700			
		16,900			

It is interesting to note that the Haber process consumes a relatively large amount of coke for the production of the hydrogen, and that any technical development of either the Bucher or modified Serpek (see p. 192) processes would be serious rivals to the Haber or cyanamide.[10]

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[6] Over nine times the value in 1914.

[7] French Patent of 1895.

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SECTION VIII.—IRON AND THE FERRO-ALLOYS

Electrolytic Iron.—The preparation of electrolytic iron has during the last few years been fairly established as a practical industrial process. There is an increasing demand for pure iron of 99·95 per cent. to 99·97 per cent. purity for the manufacture of electric machinery, where a highly inductive iron with a low hysteresis is desired, and for coating metals, *e.g.* boiler tanks, as a protection from corrosion.[1]

Iron is similar to nickel in its electrochemical behaviour. Since its electrolytic potential in *n.* ferrous ion solution is $E_h = +0{\cdot}34$ volt, and the hydrogen overpotential at the metal surface is very low, in alkaline solution $\eta = 0{\cdot}08$ volt, the deposition of hydrogen can scarcely be avoided. As in the case of nickel, the evolution of hydrogen is assisted by the cathodic passivity in the discharge of the ferrous ion.

To obtain the maximum efficiency it is therefore desirable that the ratio $C_{\ddot{Fe}}/C_{\dot{H}}$ should be kept as high as possible, provided always that basic salts are not formed; that high current densities and high temperatures should be employed to raise the hydrogen overpotential as far as possible, to increase the velocity of discharge of the ferrous ion as well as to decrease the solubility of hydrogen in the deposited metal.[2] The electrolytic deposition of iron has been developed by the firms of Mercke of Darmstadt and Langbein and Pfanhauser at Leipzig, by Cowper Coles in this country, and by Burgess in America. Both chloride and sulphate electrolytes are stated to give good results.

Chloride Electrolytes.—E. Mercke[3] employs a solution containing equal quantities of ferrous chloride and water (100 gms. of moist crystals in 75 gms. of water) warmed to 65° C. as electrolyte. Good deposits are obtained with a current density of 3 to 5 amps. per sq. dcm., provided that the electrolyte is circulated. Wrought iron anodes are employed, and the E.M.F. is about 0·60 volt. Less than 0·1 per cent. of hydrogen is occluded in the deposited metal. Langbein and Pfanhauser likewise use a chloride electrolyte containing calcium chloride in addition (700 gms. $CaCl_2$, 600 gms. $FeCl_2$ to 1 litre of water), at a higher temperature (90° C.), and with a higher current density from 15 to 20 ampères per sq. dcm.

Sulphate Electrolytes.—Burgess and Hambuechen[4] have deposited iron of 99·97 per cent. purity with a very high current efficiency (over 90 per cent.) from a ferrous ammonium sulphate solution containing 40 gms. iron per litre with the addition of ammonium chloride, at a temperature as low as 30° C. With iron anodes of Swedish bar or American ingot and a current density of 0·6 to 1 ampère per sq. dcm. an applied E.M.F. of 1 volt was found necessary to overcome the passivity at both anode and cathode. Storey[5] gives the following analysis of an iron produced under these conditions :—

Fe, 99·963 per cent. ; H_2, 0·083 per cent. ; C, 0·013 per cent.
P, 0·020 per cent. ; S, 0·001 per cent. ; Si, 0·003 per cent.

O. P. Watts[6] and H. Li find that a mixed sulphate and chloride electrolyte containing 150 gms. crystallized ferrous sulphate ($7H_2O$), and 75 gms. ferrous chloride ($4H_2O$), per litre is better than either sulphate or chloride electrolyte alone. As suitable addition agents they advised 6 gms. ammonium oxalate or 0·5 gm. hexaminetetramine (formaldehyde ammonia) per litre of electrolyte.

Other electrolytes, such as complex tartrates, citrates and oxalates, have been suggested from time to time. Classen's[7] electrolyte, containing ferrous ammonium sulphate, an equal weight of oxalic acid, and 7 times its weight of ammonium oxalate, is the only one from which carbon-free iron can be deposited and this only when the author's procedure be followed in detail.

Cowper Coles has patented the use of iron salts of several aromatic acids for the deposition of electrolytic iron.

THE ELECTROTHERMAL PRODUCTION OF IRON.

A. Ore Smelting.—Pig iron is generally produced in a blast furnace by smelting oxide of iron ores with coke or charcoal and limestone. The fuel is burnt at the base of the furnace.

The ordinary blast furnace can be conveniently divided into five zones :—

(1) The top zone, in which the entering charge is heated by the ascending hot gases. In this zone part of the carbon monoxide produced in the lower zones is oxidized to carbon dioxide—

$$2CO+O_2 \rightleftarrows 2CO_2$$

the heat liberated assisting to warm the incoming charge; to drive off the water in the ore, and convert the calcium carbonate into oxide.

(2) In this zone the ferric oxide is reduced to ferrous oxide by the carbon monoxide—

$$Fe_2O_3+2CO=2FeO+CO_2+CO$$

(3) In the third zone, where actual reduction to the metal takes place, the temperature is sufficiently high to bring about the reduction—

$$FeO+C=Fe+CO$$

The metal melted in the third zone, together with the gangue of the ore, chiefly silicious, and containing the ash of the fuel fluxed with the lime to form a fusible slag, flow to the base of the third zone, where they separate into two immiscible layers, the slag on the top of the molten metal. Both slag and pig are tapped off at intervals, fresh charge being admitted at the top of the furnace shaft.

The gases leaving the furnace are still hot (from 300° C. to 800° C.), and combustion of the carbon monoxide into carbon dioxide is not complete, the ratio CO to CO_2 being about 2 : 1. The waste gas is generally used for steam raising.

In the ideal furnace the temperature is so controlled that only the oxide of iron is reduced and not the other impurities, such as silica, manganese and the phosphates. In actual practice the phosphorus, half the manganese, and a small quantity of silicon and sulphur are retained in the iron.

The following analyses of iron ores represent those used in actual practice :—

	Limonite.	Hematite.	Magnetite.
Fe_2O_3 ..	73·840	88·500	—
Fe_3O_4 ..	—	—	78·400
MnO ..	0·567	0·470	0·700
SiO_2 ..	1·970	2·690	8·650
Al_2O_3 ..	2·152	3·470	7·330
CaO ..	0·590	0·870	2·100
MgO ..	—	—	1·030
S ..	0·070	0·078	0·055
P ..	0·124	0·093	0·008

Power Consumption.—In the production of pig iron the quantity of coke or charcoal used as fuel is about equal to the amount of pig iron produced ; charcoal of course being preferable, owing to the absence of impurities such as sulphur and silica present in the coke. In the electric furnace the carbon is used only for reduction of the oxide, and not for heating the charge; the fuel consumption is therefore reduced to about one-third of the fuel required for blast furnace operation. To heat the charge electrical energy has to be supplied, and in good modern practice 2000 kw. hours will produce one ton of pig. If we assume that the working costs of the two systems are the same and that the same quality of pig is produced, electric smelting will become cheaper than blast furnace pig when 2000 kw. hours of electrical energy cost less than 0·66 ton of high-grade coke or charcoal.

The thermochemical data necessary for calculating more accurately the theoretical efficiency of the ore-smelting process can be broadly summarized as follows[8] :—

If we take an ore containing 90 per cent. Fe_2O_3, 2 per cent. of water, and 8 per cent. of other impurities, and find by experiment that an easily tappable slag is obtained by the addition of 12 per cent. of limestone to each ton of ore in the charge, we can calculate the necessary energy expenditure for this reduction. It necessarily follows that if lower-grade ores are used, more flux will be required and a corresponding increase in wasted energy for slag production will result.

The heat of production of one metric ton of iron according to the equations—

$$Fe_2O_3+CO=2FeO+CO_2$$
$$2FeO+2C=2Fe+2CO$$

is found equal to—

$$\frac{(Fe_2,O_3)-(C,O_2)-(C,O)}{2} \text{ calories per kilomol.}$$

Since—
$$(Fe_2,O_3)=201{,}000 \text{ calories}$$
$$(C,O_2)= 97{,}200 \quad ,,$$
$$(C,O) = 29{,}200 \quad ,,$$

the energy required per metric ton of metal is 565,250 calories.

To heat the iron so produced up to the melting-point, to melt it and to bring it to the tapping temperature, a further 350,000 calories are required.

For each ton of molten pig produced (from 1·6 tons of ore) 200 kgms. of limestone will be required.

For calcining 200 kgms. of limestone approximately 85,000 calories will be required, and 240 kgms. of slag will be produced (112 kgms. CaO+128 kgms. other impurities in the ore). For reducing the impurities, heating and melting the slag to bring it up to tapping temperature, 600×240=144,000 calories will be required. The total heat required for slag formation is therefore 239,000 calories.

If we assume that the gases leave the furnace at 500° C. and contain carbon monoxide and dioxide in the ratio of

2 : 1, the energy carried off by the gases can be calculated as follows :—

For every kilomol of metal 1 kilomol of carbon monoxide and 0·5 kilomol of carbon dioxide are produced according to the equations given above. Taking the molecular specific heat of CO as 6·9 and of CO_2 as 10·0, the heat lost in the gas is $500 \times 6{\cdot}9$ calories in the CO and $\frac{500 \times 10}{2}$ calories in the CO_2, or per metric ton of pig produced 53,000 calories in the CO and 38,500 in the CO_2, a total of 91,500 calories. To this must be added the energy available in the subsequent combustion of the carbon monoxide present in the gas, viz. 68,000 calories per kilomol, or 1,046,000 calories per metric ton of pig, and the heat lost in the evaporation of the 2 per cent. of water and superheating the steam to 500° C., *i.e.* $\frac{2 \times 1{\cdot}6}{100} \times 637 \times 1000 + \frac{2 \times 1{\cdot}6}{100} \times 400 \times 0{\cdot}48 \times 1000$ $= 30{,}000$ calories, making a total of 1,167,500 calories.

Hence, for the production of one ton of pig from iron ore of the composition indicated above, the distribution of the energy required is as follows :—

Total energy required for the production of the metal	915,250	cals.
Total energy required for the production of the slag	239,000	,,
Total energy lost in the gases	1,167,500	,,
Total ..	2,321,750	,,

For every kilomol of metal produced 1 kilomol of carbon is theoretically required, or per metric ton of pig 214 kilos of carbon.

For calculating the total energy required for the production of 1 metric ton of pig, we have the following figures :—

Energy required for metal production ..	915,250	cals.
Energy required for slag production ..	239,000	,,
Energy lost as heat in the gases	121,000	,,
Total ..	1,275,250	,,

equivalent to 1500 kw. hours for a very high grade ore.

If fuel be used for heating the furnace, air must be injected for supplying the oxygen; the resulting gas will therefore contain large quantities of nitrogen, and owing to its greater velocity will leave the furnace at a higher temperature, viz. 900° C. If we assume that fractional combustion of the carbon proceeds to the same $CO_2 : CO$ ratio, viz. 1 : 2, as in the electric furnace, we shall require sufficient air to complete the following reaction:—

$$3C+8N_2+2O_2=8N_2+2CO+CO_2$$

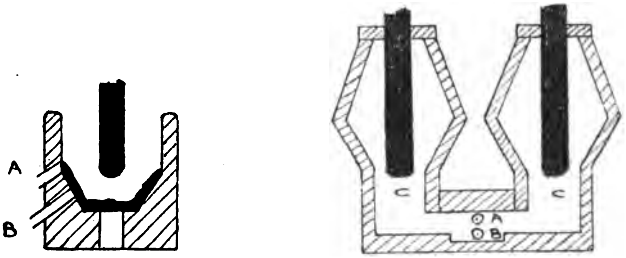
The heat liberated by the combustion of 3 kilomols of carbon to CO and CO_2 in the above ratio is 155,600 calories, and the heat absorbed by the gases leaving at 900° C., taking the molecular specific heat of nitrogen as 7, is 72,000 calories, giving a net heat of combustion for 3 kilomols of carbon of 83,000 calories. To produce 1,275,250 calories we would therefore require 550 kilos of carbon; for reduction of the iron oxide we have seen that 214 kilos of carbon are required, making a total of 764 kilos.

In this case the total energy lost in the gases owing to the increased production of carbon monoxide is much greater, viz. 4,390,000 calories, than when electrical heating is used.

As to how much of the available heat in the effluent gases can be feasibly utilized for preheating or power production wide variations are found in practice. It will be noted that in the electrothermal process 50 per cent. of the total energy supplied electrically and as fuel is thus lost. In the usual thermal process, over four times the quantity requisite for the actual smelting operation is lost. The gaseous products from the electric furnace consist of practically a pure CO and CO_2 mixture, whilst the blast furnace gas is diluted down with a large amount of nitrogen, the gas in the first case consisting of two-thirds combustible CO, with one-third of diluent, while in the second only two-elevenths combustible CO with nine-elevenths of diluent.

Furnaces.—The earliest successful furnaces employed for the production of pig iron were those of Keller and Héroult, originally used for the production of ferro-alloys.

The Keller furnace consists of two pendent electrodes in vertical shafts communicating by a passage, CC. The charge is fed in through hoppers placed round the electrodes, and provision is made for drawing off the escaping gases. Two tapping holes are provided, one for the metal, B, and the other for the slag, A. A basic dolomite lining bound with tar was found the most convenient lining. In Dr. Haanel's report to the Canadian Government (1904), he details an experimental furnace at Livet (France), where over 30 tons of ore were smelted during his visit. Using a good quality of hematite ore (48·1 per cent. iron), he was able to produce either white or grey cast iron at will, exceedingly low in sulphur, with an energy expenditure of 2200 kw. hours per ton, using 360 kgms. of 91 per cent. carbon coke and 0·17 kgm. of carbon electrode.



(A) Héroult (B) Keller

FIG. 21.—Furnaces for the production of pig iron and ferro-alloys.

In the Héroult furnace but one pendent electrode is employed. A carbon base plate continued as a liner to a little above the level of the slag serves as the other electrode. Slag and metal are removed by the tapping holes A and B. During the period of smelting fresh charge is fed in round the electrode, which is gradually raised. Dr. Haanel reported favourably on this furnace in operation at Sault Ste Marie (U.S.A.), producing pig iron from such ores as hematite, magnetite, pyrrhotite and titaniferous iron ores with the following energy expenditures :—

Hematite ..	1800	power consumption per ton pig in kw. hrs.
Magnetite ..	1900	,, ,, ,, ,,
Pyrrhotite ..	2570	,, ,, ,, ,,
Titaniferous iron ore	3500	,, ,, ,, ,,

Using low-grade charcoal as a reducing agent, 500 kgms. per metric ton of pig produced were required. The electrode consumption varied from 14 to 16 kgms. per ton of pig.

Modifications of the Keller and Héroult furnaces have been introduced by Harmet, Haanel, Stansfield, and others, but these do not include any radical change from the original designs.

Shaft Furnaces.—A distinct advance in the design of furnaces for iron ore reduction was introduced by Lyon in California and Grönwall, Lindblad and Stalhane in Sweden, who realized that the construction of large units in which the shafts were practically obstructed by the electrodes was impracticable.

Lyon's earliest types of furnace were modifications of Héroult's in which a series of pendent electrodes passing through the roof of a smelting chamber alternated with charging hoppers for supplying fresh charge. Preheating of the charge was attempted by burning the carbon monoxide evolved from the smelting charge round the hoppers. Although difficulties in operation, such as the blocking of the hoppers by the heated ore, led to a fresh series of experiments on the lines indicated by the Swedish engineers, yet this type of furnace is in operation in California by the Nobel Electric Steel Co., and by Helfenstein. It is stated[9] that the power consumption per metric ton of pig varies from 2200 to 3000 kw. hours, using a magnetite ore containing some 70 per cent. of iron and 400 kgms. of charcoal per ton of pig produced.

In Sweden, preliminary experiments by Messrs. Grönwall

Lindblad and Stalhane at Domnarfvet led to the erection of a series of large shaft furnaces at Trolhätten. These operated in a highly satisfactory manner, and furnaces of this design were subsequently erected at Hagfors in Sweden and at Hardanger and Arendal in Norway in varying sizes, from 3000 kw. to 7500 kw. per furnace.

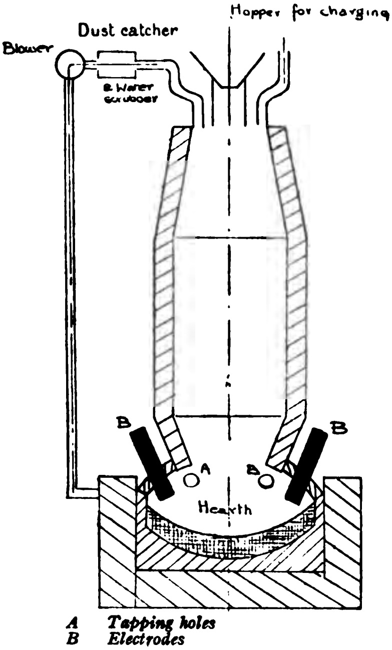


FIG. 22.—Shaft furnace for pig iron.

The furnace shaft is 15 metres high, whilst the hearth has a maximum diameter of 4 metres and is 2 metres high, constricted to a diameter of 1 metre 25 cms. where it enters the shaft. Both shaft, roof and hearth are constructed of a steel shell lined with fire-brick, with an inner lining of magnesite bound with tar.

Four or six equally spaced electrodes 60 cms. in diameter serve to conduct the current to the hearth.

Three-phase current is used, transformed at the furnace from 10,000 to 50 to 90 volts pressure and 12,000 to 20,000 ampères on each phase. The thermal efficiency of these furnaces is stated to be nearly 80 per cent., and an output of nearly one ton of pig per hour can be obtained. The fuel consumption per ton of pig produced is from 0·3 to 0·7 of a ton with an electrode consumption of 4–5 kgms. for reduction of a magnetite ore (50–60 per cent. iron). Provision is made for removing the dust and scrubbing part or all of the evolved gases, which consist of carbon monoxide and dioxide in the ratio 2 : 1, together with a little hydrogen and a smaller quantity of nitrogen. The clean gas is returned by means of a blower to the hearth through tuyeres, whilst the unscrubbed excess gas is piped away and used for steam raising. A high carbon dioxide content has a deleterious effect on the electrodes owing to partial combustion of the carbon, according to the reaction—

$$C+CO_2 \rightarrow 2CO$$

The power consumption of these furnaces averages 2200 kw. hours per metric ton of pig iron. A very high grade material is produced analyzing some 3·5 per cent. carbon, with sulphur and phosphorus usually less than 0·01 per cent. The silicon content varies with the nature of the ore, but can be usually maintained at less than 0·5 per cent. It is extremely probable that future development of ore reduction furnaces will be on the lines of the shaft type, with circulation of the gases. Under the present conditions of operation, the quantity of heat abstracted from the smelting chamber and carried to the charge in the shaft by the gas circulated is not sufficient to preheat the charge to the same degree as in the ordinary blast furnace, and furthermore, the chilling of the smelting chamber is an obvious disadvantage. It is evident that if air were injected together with some of the liberated gas through tuyeres situated just above the smelting chamber itself, the heat of combustion of the carbon monoxide could be more usefully employed inside the furnace than outside for steam raising.

B. The Production and Refining of Steel.

Although the application of the electric furnace for the production of pig iron has been slow in development and is still confined to areas where the price of electric power is very low, the electrical production and refining of steel is already a large industry, and in time will probably entirely supplant the open hearth and Martin processes.

Electrical furnaces are employed for several distinct purposes :—

(*a*) Refining open hearth and Bessemer or acid converter steel with the aid of a flux.

(*b*) Fusion of pure materials.

(*c*) Fusion of pig iron, scrap steel with fluxes, with or without the addition of oxide of iron.

Power Consumption.—Neumann[10] has calculated the necessary energy consumption for the production of one metric ton of steel, using various raw materials. When the charge is inserted cold, the energy supplied includes that necessary to heat the charge to the melting-point, to melt it and raise it to the tapping temperature, and to reduce any oxide of iron present. He further assumes the pig iron to contain 3·6 per cent. carbon, 1·68 per cent. silicon, 1·1 per cent. manganese, and 0·02 per cent. phosphorus, and the steel produced to contain 0·96 per cent. carbon and 0·28 per cent. silicon. The heat of oxidation of these impurities is subtracted from energy necessary for the refining.

Materials used.	Kw. hrs. per metric ton of steel.
Cold pig iron and flux	500
Liquid pig and flux	190
670 kgms. pig 210 kgms. ore, cold 45 kgms. lime 285 kgms. scrap	460
Same charge molten	230
675 kgms. pig 350 kgms. scrap, cold	280
Same charge molten	53
365 kgms. pig 650 kgms. scrap, cold	330
Same charge with molten pig	210

The Function of the Slag.[11]—The process of steel refining is intimately bound up with the reactions which occur both in the steel and in the slag. The metal and the slag above it form two separate phases, and in the course of purification homogeneous reactions may take place in each phase, whilst heterogeneous reactions at the surface of contact take place between slag and metal. The slag functions both as a protector and as a refiner to the underlying metal. Both sets of reactions require a high temperature to ensure a high diffusivity and a low viscosity. The ease with which a high temperature is obtained is one of the distinct advantages of the electrothermal processes. The upper limit of the temperature is set by the boiling-point of the metal, when mingling of the slag and metal occurs, taking a long time to separate.

The chief impurities, phosphorus, sulphur, and silicon, are removed by a varied series of chemical reactions, amongst which the following are most important: —

Dephosphorization.—The removal of the three chief impurities, phosphorus, oxygen and sulphur, usually takes place in the order named. Phosphorus is removed by selective oxidation at low temperatures; at 1350° C. it can be more easily oxidized than either silicon or carbon. Oxidation is brought about by the ferric oxide which is present in the slag at the period of its formation. As in the case of sulphur, the phosphorus is distributed between the slag and the metal in a definite ratio, consequently when it is oxidized in the slag, more phosphorus enters from the metal. The oxidized phosphorus is retained in the slag if basic as calcium phosphate.

During the process of phosphorus removal, part of the sulphur may be volatilized as sulphur dioxide.

Deoxidation.—When the removal of phosphorus is complete and the temperature is elevated, the ferric and ferrous oxide together with any manganese and nickel oxides and at high temperatures the oxides of chromium, tungsten and vanadium in the slag are reduced by the carbon to the respective metals, which then return to the metal phase. Silicon oxide is only reduced at very high temperatures. Any oxide of iron in the metal is continuously absorbed by the slag owing to the disturbance of the partition equilibrium, and is there reduced to metal. Part of the oxide can also be reduced in the metallic phase itself. To remove the last traces of oxide rapidly, various reducing agents can be added to the metal and the oxide formed slagged off. Aluminium, silicon as ferrosilicon and calcium carbide have all been used for this purpose. It is evident that during this period of reduction there exists a danger of phosphorus being returned to the metal from the slag by reduction of the phosphate. This can be obviated by removal of the dephosphorizing slag before reduction, or by rapidly raising the temperature during the actual reduction period to form the endothermic calcium phosphide, Ca_3P_2, which is not reabsorbed by the steel.

Both sulphur and phosphorus require basic slags to effect their removal, but the removal of oxygen can be effected in an acid slag using a silica brick lining.

Desulphurization.—The sulphur present in the original iron divides itself between the slag and the molten metal in a definite ratio in accordance with the general principles of the partition coefficient; since the ratio

$$\frac{\text{solubility of FeS in slag}}{\text{solubility of FeS in metal}}$$

increases with rising temperature, a high temperature for sulphur removal is essential. Removal of the sulphur is partly effected by oxidation to sulphur dioxide, during the period of phosphorus removal, but chiefly due to reactions taking place in the slag; more sulphur diffusing from the metal to re-establish equilibrium. Desulphurization is brought about in the slag by means of silicon, carbon, lime and carbide according to the temperature of the melt. Silicon is most active at lower temperatures, whilst carbide formation and desulphurization by means of the carbide formed only occurs at very high temperatures. When lime is used as a desulphurizing agent a large excess must be present, since the reaction—

$$CaO + FeS \rightleftarrows FeO + CaS$$

is a reversible one. The elimination of sulphur is practically complete at high temperatures, when carbide is formed owing to the removal of the ferrous oxide from the slag—

$$2CaO + 2FeS + CaC_2 \rightarrow 2CO + 2CaS + 2Fe$$

Prior to this the usual reaction—

$$CaO + FeS + C = CO + Fe + CaS$$

takes place. At low temperatures the ferrous oxide in the slag can only be removed by means of an added reducing agent, such as silicon, usually added in the form of ferrosilicon. This entails an extra expense, and may cause too much silicon to be present in the resulting steel. The intermediate formation of silicon sulphide—

$$2FeS + Si = SiS_2 + 2Fe$$

probably also plays a part in the removal of sulphur by added ferrosilicon.

Composition of the Slag.—Liquid steel leaves the furnace at about 1550° C. to 1600° C., and in the furnace itself the temperature attained lies probably between 1600° C. and 1700° C. during the last period of sulphur removal. At these temperatures the slag must be perfectly fluid, since unnecessary elevation of the temperature shortens the life of the furnace lining. In normal furnace operation the softening point of slags lies between 1200° C. and 1400° C. The work on the composition and melting-points of the various materials used for liners has largely been accomplished by the Geophysical Laboratory at Washington, but not so much work has been accomplished on the influence of the composition on the melting-point and viscosity of the slags themselves.

Vogt and Doelter[12] showed that excess of lime or silica in the slag raised the viscosity, whilst the addition of calcium fluoride made slags more fluid. In the electric furnace a 75 per cent. lime slag is still tappable. Recently the Bureau of Mines, Washington, have been investigating this problem, and a preliminary report has been given by Feild.[13] He gives the following data of the softening-points of various technical slags:—

Per cent. composition.						Softening temperature °C.
SiO_2.	Al_2O_3.	CaO.	MgO.	CaS.	MnO.	
48	8	32	5	2·0	0·1	1244
44	9	40	2	2·7	0·2	1279
38	10	40	4	3·1	1·2	1262
38	9	43	2	2·4	0·2	1263

Per cent. composition.						Softening temperature °C.
SiO_2.	Al_2O_3.	CaO.	MgO.	CaS.	MnO.	
37	11	25	20	3·5	2·2	1297
36	12	41	6	3·1	0·7	1331
35	11	42	7	3·6	0·5	1352
34	27	27	6	4·9	0·3	1342
34	14	41	6	3·4	0·6	1343
34	12	43	6	3·2	0·5	1358
34	15	38	10	2·9	0·3	1365
32	16	44	1	4·4	0·1	1356
32	12	45	6	3·4	0·5	1383
32	11	44	4	5·9	0·5	1425
32	15	48	2	3·5	0·2	1403
31	15	36	10	5·5	0·2	1388
18	35	31	10	4·1	0·3	1410

He determined the tapping temperature of various slags and found it to lie between 1470 and 1572° C. as determined by optical pyrometer and also by thermocouple. The figures refer to blast furnace slags, and, as we have noted, the temperature in the electric furnace is considerably higher. The average viscosity of the slags at 1500° C. was found to be about 301 times greater than that of water at 20° C.

The pure silicates have the following melting-points :—

$FeSiO_3$	1050° C.
$MnSiO_3$	1150° C.
$CaSiO_3$	1200° C.
Mg_2SiO_4	1400° C.

Types of Furnaces employed.—Three types of furnaces have been employed for steel production and refining, viz. the Arc, Induction, and Resistance furnaces, but only the two former are in operation on a large scale. The arc and induction furnaces have each distinct advantages but at the same time have faults peculiar more to the principle of heating than to the actual type of furnace employed. In the induction furnace the metal is relatively hotter than the slag, although it never actually attains the temperatures obtained in the arc furnace.

In addition, owing to the action of the electromagnetic field the fluid metal is always moving, and a very intimate slag metal contact is produced. In the arc furnace the slag is relatively hotter than the metal. It consequently follows that homogeneous slag reactions proceed best in the arc furnaces, and the heterogeneous metal slag reactions in the induction type.

Dephosphorization, which proceeds with a reasonable velocity at relatively low temperatures, is usually not complete in the arc furnace, but proceeds most smoothly in the inductance. For the removal of sulphur where high temperatures of slag and metal and a perfectly reducing atmosphere are desirable, the arc offers advantages over the inductance type. Furthermore, although the latter requires less attention than the former, it suffers from the additional disadvantage of possible emulsification of the slag in the liquid metal, owing to the spin produced by the electromagnetic field.

Arc Furnaces.—Of the more important types of arc furnaces employed may be mentioned the Girod, the Héroult, Keller and Stassano's.

The *Girod*[14] furnace is representative of the conducting hearth furnace in which the current passes from one or more pendent electrodes through the slag and metal to the hearth. A combination of arc and resistance heating is thus obtained.

A good number of furnaces of this type are at present in operation in Europe and America, from ½ ton up to 12 tons capacity. Even larger sizes are in contemplation.

The lining of the furnace is usually calcined magnesia or dolomite bound with pitch. If the temperature be carefully controlled it is stated that nearly 100 charges can be run without the necessity of any repairs. The furnace cover lasts some twenty charges.

The labour cost is small, since three men can operate a 12-ton unit. In this size the power consumption is some 800 kw. hours per metric ton of steel when starting up from cold materials.

The carbons, of which there are four pendent ones, are 35 cms. in diameter, connected in parallel, and the furnace operates at 70 to 75 volts with a current of 4000 ampères per carbon. The average carbon consumption is about 6 kgms. per ton of steel.

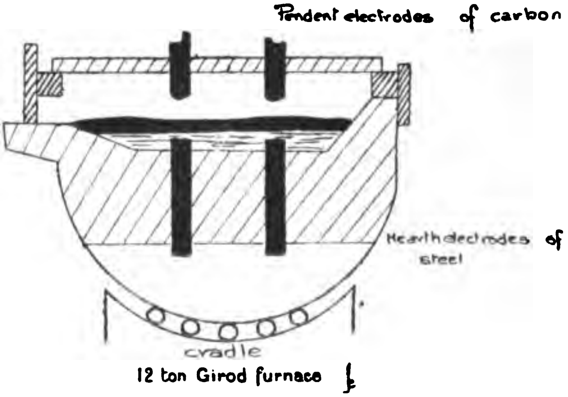


FIG. 23.—Conducting hearth furnace for steel production.

Less load fluctuation is obtained in this type of arc furnace, but it would appear that the furnace lining has to stand severer treatment than that which obtains in the Héroult or Stassano series arc types.

The *Héroult* and *Keller* furnaces are of the series arc type, in which the current passes from one electrode to the other through the metal, striking arcs between metal and electrodes in its passage. Frequently three pendent electrodes are used for three phase-current, whilst Keller has used four electrodes for simple alternating current. The use of six electrodes in one hearth for three-phase current has been suggested.

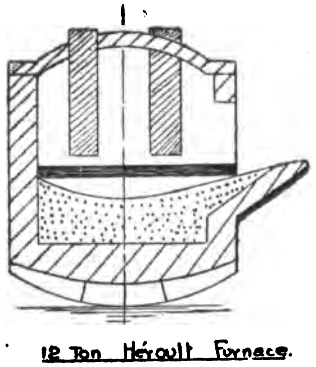


FIG. 24.—Series arc furnace for steel production.

The furnace follows the normal construction, consisting of a steel shell with a magnesite or dolomite lining. The roof liner is frequently made of silica brick. Since no hearth electrode is employed, the liner may be further protected by a magnesite slag mixture bound with pitch.

The voltage lies between 90 and 100 volts, and the power consumption per metric ton of steel produced with a cold charge is from 700 to 800 kw. hours, and with a hot one from 200 to 300 kw. hours. The electrodes are usually very large, to reflect the arc down on to the surface of the slag and thus protect the roof liner; up to 60 cms. diameter electrodes have actually been used. The electrode loss is naturally heavier than in the Girod type, being about 12 kgms. per ton of steel produced.

These furnaces have been put to a variety of uses. At Chicago,[15] Bessemer converter steel is blown until the carbon and silicon are practically all removed. The metal is then poured into the electric furnace, and lime and iron ore are added to remove the phosphorus. At the end of half an hour the furnace is tilted, the slag removed, and a fresh flux of lime, fluorspar and coke is added to remove oxygen and sulphur. When the removal is complete, the suitable amounts of carbon, ferrosilicon and ferromanganese are added, the furnace is again tilted, and the metal run from the ladle into the moulds.

At Syracuse, phosphorus and carbon are removed in an open hearth furnace and the molten metal subsequently transferred to a Héroult furnace for desulphurization.

At La Praz, three slags are formed and removed before the final addition of the requisite amounts of ferro-alloy and carbon are made to the steel.

Each slag removal necessitates the supply of an additional 50 to 60 kw. hours per ton of steel produced.

Stassano's Furnace.—Captain Stassano in Italy was one of the first investigators into the possibility of smelting iron ores in the electric furnace. After a series of experimental runs at Cerchi, large electric smelting plants were installed at Darfo and Turin. He endeavoured to produce steel in one operation directly from the ore. It is evident that for the further refinement and decarburization of the pig iron usually produced, provision must be made for the supply of only the requisite amount of carbon and no more. In addition the molten pig must be retained in the furnace in such a manner that the heterogeneous metal slag reactions, by which the actual process of purification is accomplished, have time to complete themselves.

Stassano accomplished the first by careful analysis of the high-grade ore employed and briquetting it with the requisite amount of carbon and flux, using pitch or water glass as a binding material. The furnace itself consists of a magnesia-lined cylinder with a domed roof capable of slow revolution around a nearly vertical axis. Horizontal electrodes, three or four in number, are employed, being diametrically introduced at the centre of the furnace cavity and slightly inclined to the horizontal.

The briquetted charge is introduced at the top of the furnace, and two tapping holes are provided for the withdrawal of the metal and slag. At the commencement of the operation a short arc is employed, but as the temperature within the furnace rises the arc gap becomes more conducting owing to the volatilization of impurities, and the electrodes are withdrawn until an arc of some 40 to 50 cms. long is obtained. Since the arc does not make any contact with the ore or metal, heating is accomplished by radiation alone.

With a magnetite ore containing 48 to 50 per cent. of iron 1 metric ton of metal could be produced with an energy expenditure of 4800 to 5900 kw. hours, and an electrode consumption of 10 to 15 kgms.

Various analyses of the resulting metal have been given [16] both by Stassano and by other investigators. The following may be taken as the extreme limits of the carbon content:—

	Per cent. composition.	
	(1)	(2)
Carbon	0·80	0·090
Manganese	0·30	0·092
Silicon	0·22	Trace
Phosphorus	0·015	0·009
Sulphur	0·045	0·009

The process has not extended beyond the confines of Italy.

Induction Furnaces.—*The Kjellin Furnace.* This furnace consists essentially of a step-down transformer in which the secondary winding is replaced by an annular trough of refractory material containing the molten steel, A, A. This is excited by the primary B, B, and the lines of force are retained as far as possible in the system by the thin sheet-iron laminated core C, C.

The first furnace of this type was installed at Gyringe in Sweden. With a primary alternating current of 90 ampères at 3000 volts, the estimated induced current was 30,000 ampères at 7 volts. The power consumption was found to be 800 kw. hours per ton when charged with cold metal, and 650 kw. hours per ton when charged hot. Lindblad uses the following formula for determining the power factor :—

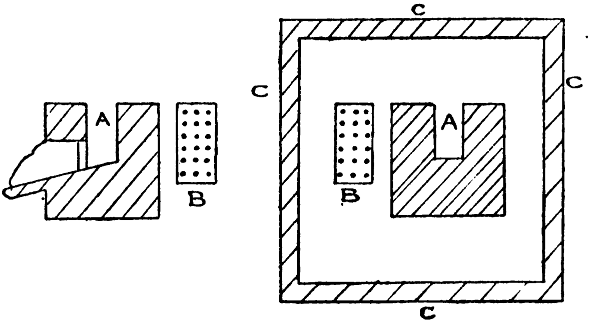


FIG. 25.—Kjellin induction furnace.

$$\left(\frac{1-p^2}{p^2}\right)^{\frac{1}{2}}=\frac{Cna}{ls}\left(\frac{1}{W^s}+\frac{1}{W^p}\right)$$

where p=the power factor.
n=the frequency.
$\frac{a}{l}$=the ratio of area to length of the steel in the channel.
s=the sp. resistance of the steel.
C=a constant.
W^s and W^p=the magnetic resistances of the two circuits.

The power factor is consequently greatest when the right-hand term is small. It would therefore appear necessary to have a very low frequency current employing a high secondary resistance in the form of a long thin trough.

The furnace referred to operated on a current of frequency 13·5 cycles per second, having a power factor as low as 0·635. A further disadvantage is to be found in the fact that the secondary cannot be completely emptied of metal, if it be desired to keep the furnace warm prior to the insertion of a fresh charge. If a hot charge be placed in the furnace its capacity is considerably augmented.

In the Colby and Grönwall furnaces, these difficulties are partly overcome. Colby utilizes a water-cooled coiled pipe as primary circuit, permitting of it being placed in closer proximity to the secondary. A power factor of 0·90 to 0·93 is claimed, and the calculated power comsumption per ton of steel is 590 kw. hours for a cold charge and 490 kw. hours for a hot one. In Grönwall's furnace, a long serpentine trough is used in order to ensure a high resistance in the secondary circuit; a high power factor is claimed.

In spite of the disadvantages of the simple induction furnaces such as the low power factor with currents of normal frequency, together with the difficulty of protecting a long trough of molten metal from excessive heat radiation, several of the Kjellin type have been employed, usually for the preparation of special steels and ferro-alloys in which simple fusion operations are required, where local overheating is to be avoided, and no slag formation is desired. The slag is not usually sufficiently heated, and its removal from the annular trough is a matter of considerable difficulty.

Frick furnaces, which are simple modifications of the Kjellin, are in operation at Krupp's works at Essen for the production of ferromanganese and melting scrap.

The following figures have been published relating to these furnaces:—

	Kw. hrs. per ton.
Ferromanganese production	600
Melting scrap	587
Steel refining	90

Composite Furnaces.—The most successful composite furnace employed in the preparation of steel is the Röchling Rodenhauser resistance induction furnace.

In these furnaces the laminated soft iron cores A, A, with the primary windings B, B, are surrounded by the secondary molten-metal troughs D which are protected by the magnesia-lined fireclay walls CE. The troughs meet in a common space between the two cores, and a large reservoir of molten metal is thus provided.

The heating of the metal in the trough is provided by means of the induced current, but an extra supply of energy has to be supplied to maintain the reservoir at the desired temperature. This is accomplished by means of a few turns of heavy cable wound round the pole pieces and connected to iron plates F, F, embedded in the magnesia liner E, E, at the opposite ends of the trough. The magnesia becomes sufficiently conducting at high temperatures to permit of the passage of the current induced in the cable through the molten steel. About 65 per cent. of the induced current goes through the annular troughs, and the remaining 35 per cent. through the central reservoir.

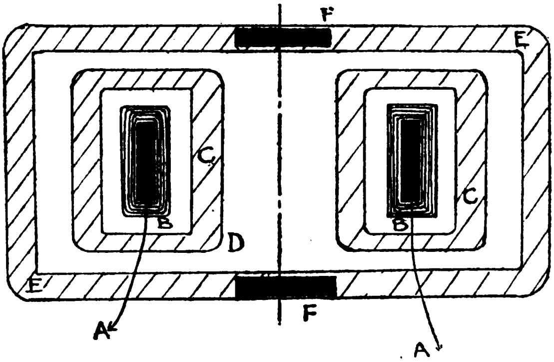


Fig. 26.—Röchling Rodenhauser resistance induction furnace.

Furnaces of this design have been built up to 8 tons capacity, and have been found suitable for both preparing and refining steel. The difficulties associated with the electromagnetic rotation of the molten metal when three-phase current is employed have already been referred to.

To overcome the chief objection raised against this furnace, viz. the low temperature of the slag, small arc electrodes have been suggested as supplementary slag heaters, as in the Paragon and Nathusius furnaces, the requisite power being naturally obtained by an additional secondary winding on the cores.

Although more expensive to erect, the induction furnaces offer considerable advantages over the arc type, inasmuch as no expense is entailed for carbon renewal, perfectly gas-free metal can be obtained, and no impurities from carbon ash are dissolved by the metal. The wear on the lining due to the electromagnetically produced spin in the metal is somewhat heavy.

Miscellaneous Furnaces.—Resistance furnaces such as those of Gin[17] have not proved suitable for steel refining, owing to the very high currents employed necessitated by the low resistance of the molten metal.

Two interesting types of furnaces which have not yet been applied on a technical scale may be mentioned, since the application of the principles employed are novel for the purpose in view, and laboratory experiments have yielded highly satisfactory results.

The Hering "Pinch" Effect Furnace.[18]—Hering, when investigating the operation of the Kjellin furnace, noticed that when high current densities were employed the surface of the metal became occasionally depressed; ultimately the ring was divided and the current ceased. He pointed out that the depression was caused by the pressure directed towards the axis caused by the mutual attraction of the coaxial cylinders of metal carrying the induced currents. Northup has shown that this pressure exerted perpendicularly to the axis of the cylinder is proportional to the square of the current and inversely to the square of the radius. Consequently any slight difference in diameter of the fluid metallic conductor will produce a great alteration in the axial pressure. Under these conditions the fluid will be forced from the constricted area, thus increasing the "pinch" effect, and a ruption will ultimately result Hering has applied the "pinch" effect to a small-scale furnace with success.

The molten metal contained in a reservoir is connected to water-cooled electrodes through two narrow channels containing some of the molten metal, which in turn are connected to the secondary winding of a transformer. Very active circulation of the metal is caused by the continuous "pinching" of the metal in the tubes. Heating accomplished by the passage of the current from the secondary, according to Hering, is slightly augmented by the frictional heating in the tubes. The furnace has been employed successfully as a crucible furnace for steel melting, and preliminary experiments have been made on the direct production of pig iron.

It is evident that the furnace thus designed should possess considerable advantages over the ordinary induction furnace. The rapid circulation of the metal ensures a uniform temperature distribution, and should considerably accelerate slag metal reactions owing to the continuous renewal of the surface of contact. High slag temperatures are more easily obtained owing to the fact that very thick furnace walls can be used.

Although the wear on the "pinching" channels is liable to prove excessive, and possible emulsification of the slag in the metal may occur in the channels themselves, large-scale experiments on furnaces of this design would probably give results better than those of the ordinary induction furnace, and certainly better than those given by the resistance furnaces.

Northrup's Tesla Induction Furnace.—Northrup[19] has pointed out that the limitations of the ordinary induction furnace are determined by the "pinch" effect in the fluid secondary winding, and the excessive magnetic leakage in the usually accepted annular form of construction. He has accordingly designed a crucible furnace thermally and electrically insulated on the outside; this is wound with about fifty turns of wire, which serve as the primary of the induction coil. The ends of this primary are connected to the electrodes of a Tesla coil fitted with condensers and capable of providing very high voltage oscillating discharges. The metal in the crucible serves as the secondary of the coil. A 20-kw. furnace has been constructed and found to operate successfully with a condenser terminal voltage of 5400 to 7200 volts, and the natural period of oscillation of the discharge. The thermal efficiency is stated to be 60 per cent., a high figure when the small size of the furnace is considered.

C. The Ferro-alloys.

The production of ferro-alloys in the electric furnace was one of the earliest applications of electrothermal methods to the preparation of iron and steel. Amongst the most important alloys manufactured may be mentioned ferro-silicon, ferro-tungsten, manganese, chrome, molybdenum and smaller quantities of ferro-uranium and titanium.

Ferro-silicon.—Arc furnaces are generally employed for the production of ferro-alloys, either with a basal electrode such as the Héroult, in which combined arc and resistance heating are employed, or the series arc type as in the Keller (p. 212).

In the preparation of ferro-silicon originally iron ore was used, but scrap iron is now employed. It is made in several grades, containing 25 per cent., 50 per cent., 75 per cent., and over 90 per cent. silicon. The preparation of the purer silicon grade has already been described.

Ferro-silicon should be prepared from scrap iron of low phosphorus content, since the presence of calcium phosphide has been shown to be the source of explosions and cases of poisoning, formerly of frequent occurrence in the manufacture and handling of the substance. Ferro-silicon containing over 70 per cent. silicon is more stable than the lower grades. The raw materials used are crushed quartz and carbon in the form of anthracite or coke. Sand has also been experimented with, but is liable to choke the furnace.

The furnace charge crushed to a small size should contain sufficient carbon to reduce the quartz, according to the equation—

$$SiO_2+3C=2CO+Si$$

and iron is added in amount depending on the grade of ferro-silicon required.

The voltage employed with a single-arc furnace varies from 70 to 75 volts, and the power consumption for a 75 per cent. grade ferro-silicon is roughly 5000 kw. hours per metric ton, for a 30 per cent. ferro-silicon only 3500 kw. hours are necessary.

About 80 per cent. of the charge is converted into utilizable ferro-silicon; the remainder is used for slagging off the impurities in the quartz and coke. Ferro-silicon absorbs very little carbon during the process of formation, and furnace liners of carbon are frequently employed.

Attempts, partly successful, have been made to utilize blast furnace slags,[20] and ordinary sandstone[21] rock as source of the silica.

An application of the electric furnace has recently been made to the preparation of special ferro-silicon and silicized iron having resistant properties, probably associated with the formation of superficial layers of iron silicides, $FeSi_4$ and $FeSi_2$.

Owing to the stimulus given by the war to the production of strong acids, a great number of these non-corroding castings have been introduced under a variety of names, such as Tantiron, Narki, Illenit, Neutraleisen and Metaldür. The earlier forms were exceedingly brittle, and could not be machined, but recently large castings capable of being machined have been introduced, and the presence of flaws practically eliminated.

Ferro - tungsten. — Ferro - tungsten is generally prepared on the intermittent system. The charge is fused in a simple furnace lined with clay having a pendent and one basal electrode. When the reduction is completed, the charge is allowed to solidify, and is then broken out. Attempts have also been made to use tilting furnaces to avoid the time wasted in cooling the melt.

As source of tungsten, various ores and ore concentrates are used, the most common being scheelite, $CaWO_4$. Reduction is usually accomplished by means of coke, and the iron is supplied by the addition of hematite. Sulphide of iron has also been used :[22]

$$CaWO_4+FeS+4C=(Fe,W)+CaS+4CO$$

Gin has proposed the use of ferro-silicon as a reducing agent instead of carbon, but the process does not appear economical—

$$3CaWO_4+4Fe_2Si=3CaSiO_3+FeSiO_3+(Fe,W)$$

Ferberite, Fe_2WO_4, and wolframite, $FeMnWO_4$, are other important tungsten ores, and can be directly reduced with carbon in the electric furnace, most of the manganese being volatilized at the temperature of reduction, 2800° C. The loss of tungsten in the operation of reduction is usually small, but decarburization of the alloy is usually essential owing to the formation of tungsten carbide, W_2C.

Decarburization for low-grade tungsten alloys can most easily be accomplished by the addition of a strictly limited amount of oxide of iron. Excess of iron oxide is to be avoided owing to the formation of ferrous tungstate. For higher grades, calcium carbide and ferro-silicon with a flux of calcium fluoride are employed, any silica present in the concentrates being fluxed by the addition of lime.

According to Keeney[23] the power consumption for reduction and decarburization can be reduced to under 7500 kw. hours per metric ton. Hutton[24] gives the following analyses of two typical industrial alloys :—

	Percentage composition.	
	(1)	(2)
Tungsten	85·15	71·80
Iron	14·12	24·35
Carbon	0·45	2·58
Silicon	0·13	0·36
Manganese	0·085	0·75
Sulphur	0·021	0·02
Phosphorus	0·018	0·008

Metallic tungsten and high-grade tungsten alloys are used for the production of crucible tool steels, whilst the lower grades with the higher carbon content are employed for open-hearth steels containing low percentage of the metal.

Ferro-manganese.—Ferro-manganese is usually prepared in the blast furnace,[25] but different grades of the alloy are prepared by the fusion of scrap metal and manganese in the electric furnace. As has already been indicated, induction furnaces (p. 225) appear most suitable for this work, although Héroult and Girod furnaces have been employed for the purpose.

To prevent absorption of manganese by the calcined dolomite liner, the walls are frequently protected with a tar or a mixture of retort coke and coal tar.

Ferro-chrome.—Ferro-chrome has found an increasing field for use in special steels for naval and military purposes, and also in the production of the so-called "rustless" steels, which, although malleable and capable of being welded, are resistant to sea-water and acids.

A continuous operating furnace can be employed, being tapped at the base. The furnace walls are usually lined with dolomite or magnesite, but frequently a chromite liner is employed; with careful operation, the life of a liner may exceed three years. The chief source of chromium is the mineral chromite, $FeO.Cr_2O_3$, and reduction is usually accomplished by means of carbon, although silicon, aluminium and calcium carbide have been suggested. The latter processes have not proved economically successful.

The charge of finely powdered chromite and coarse anthracite or coke in the requisite quantities to ensure reduction is fed into the furnace at regular intervals.

Reduction commences at about 1185° C.[26] By intermittent tapping a ferro-chrome containing only from 2 to 5 per cent. of carbon can be run off, although the carbon content may run considerably higher. For the purpose of preparing a low carbon ferrochrome, a decarburizing process is necessary, since the direct production of a low carbon alloy is, according to Keeney,[27] always attended by an excessive loss of chromium in the slag. Refining is usually accomplished by fusion of the alloy with a suitable slag containing chromite or oxide of iron, lime and fluorspar. Decarburization is accomplished according to the following equation :—

$$2Fe_3C+6Cr_2C_3+5FeO.Cr_2O_3=11FeCr_2+20CO$$

The carbon of the resulting alloy is usually below 0·5 per cent. and may be lower.

Hutton gives the following analysis of commercial ferro-chromium :—

	Percentage composition.
Chromium	67·05
Iron	27·05
Carbon	4·25
Silicon	0·60
Manganese	0·46
Aluminium	0·22
Magnesium	0·31
Sulphur	0·02
Phosphorus	0·02

The power consumption ranges between 6000 and 7200 kw. hours per metric ton, with an electrode loss of 25 kgms. of carbon.

Chromium-nickel alloys for the production of high speed tool metal have recently been introduced and are being prepared in increasing quantities.

Ferro-molybdenum.—Ferro-molybdenum is prepared from molybdenite ore or concentrates averaging 90 per cent. MoS_2. The correct proportions of iron turnings, anthracite, coal or coke and the raw or roasted ore, together with lime, are heated in an intermittent electric furnace, usually of the basal electrode type. Reduction takes place according to the equation—

$$2MoS_2+2CaO+3C+Fe=FeMo_2+2CaS+2CO+CS_2$$

The resulting alloy usually contains from 3 to 4 per cent. of carbon. A typical analysis is as follows :—

	Percentage composition.
Molybdenum	80·20
Iron	12·65
Sulphur	0·025
Phosphorus	0·028
Carbon	3·27

Decarburization and desulphurization can be accomplished by means of a slag containing lime and oxide of iron slag. Reduction by means of carbides, aluminium and silicon, including ferro-silicon, have all proved too expensive for commercial practice. The loss by volatilization of molybdenum oxide is frequently very high and may amount to as much as 30 per cent.

Ferro-vanadium.—The electric furnace method for preparing ferro-vanadium has only recently supplanted the more usual thermite process. A great variety of processes have been suggested for the production of the alloy, amongst which may be mentioned—

1. Fusion of a mixture of 10 parts vanadium pentoxide, 1 part of silica and 3 parts of carbon, with the requisite amount of iron.

2. Briquetting vanadium trioxide and ferro-silicon by means of tar.

3. Electrolysis with an iron cathode from a double fluoride electrolyte.

4. From ferro-vanadium silicide, SiFeV and vanadium fluoride.

5. From the oxides, reduction being brought about by means of carbon. A current of 900 ampères at 50 volts in a small arc furnace will provide an alloy containing from 4 to 6 per cent. carbon. By reheating with a limited amount of oxide the carbon content can be reduced to under 1 per cent.

The largest source of supply is the sulphide ore, patronite, and experiments by Keeney have shown that the preparation of the ferro-alloy can be accomplished in a manner similar to that employed for ferro-molybdenum.

Ferro-titanium, Uranium and Boron.—Ferro-titanium, used as a deoxidizer for cast iron, is made by smelting titaniferous iron ore with carbon or aluminium, whilst the uranium alloy has been prepared in small quantities from sodium uranate, $Na_2Ur_2O_7$, or uranium oxide, U_3O_8, by smelting with iron sulphide and lime or with oxide of iron and calcium carbide or ferrosilicon. The boron alloy is prepared by reduction of a mixture of scrap iron and borax or boric acid with carbon.

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APPENDIX

SOME ELECTROLYTIC PROPERTIES OF THE ELEMENTS

Element.	Electrolytic Potential E_h.	Electrolytic over-voltage η to H_2.	Electro-chemical equivalent wt. of metal in grms. deposited per ampère-hour.	Valency in solution.	Usual current densities employed for deposition, refining, plating in ampères per sq. decimetre.		
					Deposition.	Refining.	Plating.
Potassium	+3·20	?	1·46	1	200	—	—
Sodium ...	+2·82	?	0·86	1	Castner 200 Griesheim 1000	—	—
Barium ...	+2·82	?	2·56	2	—	—	—
Strontium	+2·77	?	1·63	2	—	—	—
Calcium ...	+2·56	?	0·75	2	10–250, contact electrode up to 10,000	—	—
Aluminium	+ ?	?	0·34	3	Hall 100 Héroult 190	—	—
Magnesium	+1·49	?	0·45	2	10–15	—	—
Molybdenum	+ ?	?	0·60	6	—	—	—
Chromium	+ ?	?	0·65	3	—	—	—
Manganese	+1·075	?	1·03	2	—	—	—
Zinc ...	+0·770	0·70	1·22	2	Sulphate electrolyte 1–50 Chloride electrolyte 3–4	0·8–1 —	0·8–1 —
Indium ...	+0·45	?	1·43	3	—	—	—
Cadmium ...	+0·42	0·48	2·09	2	—	1·4	1·0
Iron ...	+0·34	0·08	1·10	2	—	3–20	—
Thallium ...	+0·322 (in Tl solutions)	?	3·80	2	1·3–1·5	—	—
Cobalt ...	+0·232	?	1·10	2	1·0	1·0	0·3–4
Nickel ...	+0·228	0·03–0·21	1·07	2	1·0	1·0	0·3
Tellurium ...	?	?	2·38	2	—	—	—
Tin ...	+0·192	0·43–0·53	2·22	2	—	1–2	0·1–1
Lead ...	+0·148	0·35–0·64	3·86	2	—	Silicofluoride 0·9–2·2 Perchloride 2–3	—
Hydrogen ...	0	0	0·0376	1	—	—	—
Copper ...	−0·329	0·03–0·23	2·37 1·18	1 2	0·5–2	2·2	0·5–2·5
Bismuth ...	−0·393	?	2·58	3	—	—	—
Antimony ...	−0·463	?	1·49	3	0·7	—	—
Mercury ...	−0·750	0·42–0·78	7·46	2	—	—	—
Silver ...	−0·771	0·05–0·15	4·02	1	—	2–3·5	0·3
Palladium	−0·793	0·23–0·46	1·99	2	—	—	—
Platinum ...	−0·863	0·07–0·09	1·81	4	—	—	—
Gold ...	−1·05– −1·18	0·02–0·06	2·45 7·35	3 1	0·005–0·01	30	0·1–0·4

NAME INDEX

SUBJECT INDEX

THE END

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